

Current Density Mismatch in Perovskite Solar Cells

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Perovskite solar cells (PSCs) have sky-rocketed in recent years because of their high-performance, now at a certified 25.2%, as well as readily available fabrication methods and material components. They are now considered one of the main contenders to make a lasting impact in photovoltaics either as a stand-alone solution, for example on flexible substrates, or in multijunction architectures with established technologies such as silicon or CIGS.

This tremendous potential has led to an unusually rapid development of perovskite materials by academic and industrial groups. This includes a coordinated effort for certified measurement protocols.¹ For example, efficiency certifications of PSCs now consider the need for a stabilized power output because of the idiosyncratic ion migration in PSCs. Similarly, there is an effort toward the normalization of stability measurements to eventually form an industrial protocol.²

It is only logical to move toward standardization because it ensures comparability among research groups and industry. More binding measurement protocols also build credibility toward potential investors and are therefore a necessary precursor for industrialization.

Another layer of normalizing the measurement of solar cells was recently introduced by several journals^{3–5} in the form of a checklist for reporting performance parameters of solar cell. Here it is typical, among a series of requirements, to report on the discrepancy between the short-circuit current density (J_{sc}) from external quantum efficiency (EQE) ($J_{sc,EQE}$) and current density-voltage (JV) ($J_{sc,JV}$) measurements.

The EQE is a basic measurement for solar cells. It measures the conversion of an incident photon to an electron by the photovoltaic device and is in general a function of the photon wavelength. The inset of the EQE(λ) can provide the spectral regions which contribute to the photocurrent generation of the solar cell (see Figure 1). Its spectral shape reveals, for example, how efficiently an absorber material transforms light into current and may reveal loss mechanisms within the device stack.

Experimentally, the EQE can be measured with a light source, often a Xe lamp, with a monochromator. The light source is used to illuminate the sample through an appropriate shadow mask. The device is kept at short-circuit condition, and the current through the device is measured with a source meter for each wavelength.

The raw data of the current needs to be normalized to the number of incident photons, conducted by calibration of the

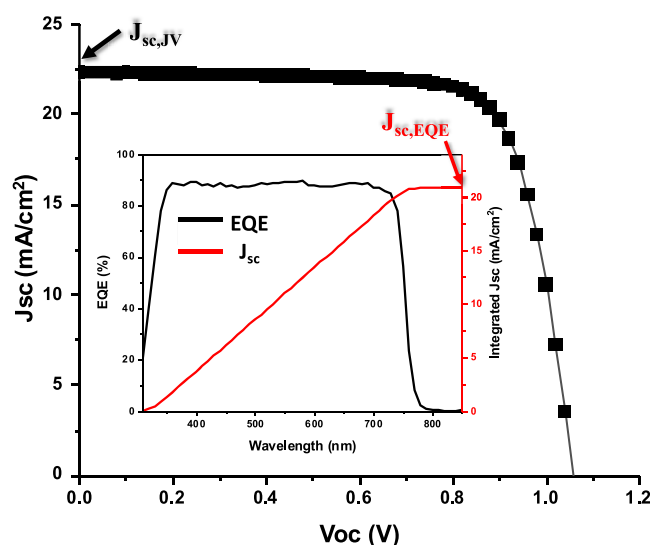


Figure 1. JV curve and EQE spectrum of a typical perovskite solar cell. The definitions of $J_{sc,JV}$ and $J_{sc,EQE}$ are shown in the figure.

setup with a reference solar cell with a known spectral response for each wavelength.

The EQE is the spectral response of the solar cell; therefore, it can be used to calculate the J_{sc} of the cell under illumination.

$$J_{sc,EQE} = \int qEQE(\lambda) S(\lambda) d\lambda \quad (1)$$

where $S(\lambda)$ is photons per second.

Typically, the J_{sc} is measured from the JV curve, which depicts the short-circuit current density as a function of applied voltage. The JV curve allows for extraction of the open-circuit voltage (V_{oc}), the fill factor (FF), and thus the power conversion efficiency (PCE). Hence, the $J_{sc,EQE}$ provides a complementary method to compare with the $J_{sc,JV}$. Figure 1 shows the definition of $J_{sc,JV}$ and $J_{sc,EQE}$. Optimally the $J_{sc,JV}$, as measured by the solar simulator, should match the $J_{sc,EQE}$.

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Comparing the two values is an important and easy check for the reliability of JV and EQE measurements, avoiding measurement errors due to wrong calibration.

In recent years it emerged that for PSCs the reported $J_{sc,EQE}$ is relatively consistently lower than the $J_{sc,JV}$. This is illustrated in Table 1, which shows certified PSCs and their respective

Table 1. Certified PCEs with FF, V_{oc} , and $J_{sc,JV}$ Extracted from the JV Curve^a

certified PCE (%)	FF	V_{oc} (V)	$J_{sc,JV}$ (mA cm^{-2})	$J_{sc,EQE}$ (mA cm^{-2})	Δ (mA cm^{-2})	ref
23.32	0.78	1.18	25.2	24.5	0.7	6
22.10	0.80	1.10	25.0	24.0	1.0	7
21.90	0.78	1.10	25.5	24.2	1.3	8
21.70	0.78	1.14	24.3	23.8	0.6	9
21.52	0.79	1.11	24.5	24.2	0.3	10
20.11	0.77	1.06	24.6	24.4	0.2	11
17.91	0.74	1.11	21.8	22.0	−0.2	12
16.15	0.74	1.11	19.6	19.3	0.3	13
14.67	0.74	1.10	18.0	17.7	0.3	14
12.84	0.66	0.86	22.8	21.1	1.7	15

^a $J_{sc,EQE}$ shows the highest reported J_{sc} value from the integrated EQE spectrum. Frequently, this is not measured directly on the certified device. The certificates never report absolute values for $J_{sc,EQE}$. $\Delta = J_{sc,JV} - J_{sc,EQE}$ shows, with the exception of one data point, that there is a consistently lower $J_{sc,EQE}$.

$J_{sc,EQE}$ and $J_{sc,JV}$. It is noteworthy that none of the certificates contain absolute values for the $J_{sc,EQE}$, although the spectral shape of the EQE is frequently reported. Thus, the reported $J_{sc,EQE}$ values are not certified and were calculated in the respective laboratories. Often, the $J_{sc,EQE}$ is close to, albeit less than, the $J_{sc,JV}$, within 10–20%, thus showing that the measurement from the JV curve is reasonably accurate. Except for one value, Table 1 shows that the $J_{sc,EQE}$ is less than the $J_{sc,JV}$.

We exemplify this discrepancy further with our own PSCs in Figure 1. The EQE measurements were taken without white light bias. The $J_{sc,JV}$ of this cell is 22.3 mA cm^{-2} , where the $J_{sc,EQE}$ is 20.9 mA cm^{-2} with a relative difference of 1.4 mA cm^{-2} , consistent with Table 1.

The calibration for absolute EQE values is notoriously tricky. A typical EQE setup uses a Xe lamp in combination with a monochromator as light source. Therefore, the light intensity at a given wavelength is low compared to the standard 1 sun illumination used in the solar simulator. As a result, the charge density in the device is different, which can increase the mismatch of the $J_{sc,JV}$ and the $J_{sc,EQE}$ of the solar cell.

This is pronounced in solar cells that show a nonlinear behavior of the photocurrent with light intensity. Such devices are usually recombination-limited.¹⁶

Moreover, if such variations were random, we would expect to observe, at least as equally often, a slightly increased $J_{sc,EQE}$ compared to $J_{sc,JV}$. However, the systematically lower $J_{sc,EQE}$ speaks to the opposite, hinting that there is an underlying reason.

The mechanism is hard to precisely pinpoint at this stage and goes beyond the scope of this Viewpoint. Nevertheless, we posit that it may be connected to the following observations/reasons or a combination thereof:

- The ion migration within the perovskite materials changes the interface dynamics during the relatively

long measurement time required to record each wavelength for the $J_{sc,EQE}$ compared to the relatively quick $J_{sc,JV}$.^{17,18}

- Long-term sample degradation may be induced by longer measurement times.¹⁹ A possible option in this case could be to reduce the measurement time and thus the effects of possible degradation of devices during measurements.
- The measurement conditions at the solar simulator are not the same as the conditions during the EQE measurement. It can be assumed that the JV sweep in the solar simulator corresponded to a prebiasing which is not the case in the EQE characterization. For example when a forward bias is applied on the perovskite solar cell, the electric field in the perovskite cell is influenced. The external bias leads to ion movement inside the perovskite layer and at the interfaces; as a result, a partial build-in potential is created, which influences the observed EQE.²⁰
- A preconditioning measurement of the cell will affect the absolute scale and the shape of the EQE. This can cause an additional discrepancy between the J_{sc} values. Moreover, often a white light bias is applied during the EQE measurement. This results in a photovoltage which can also distort the $J_{sc,EQE}$ measurement.²¹ The light bias usually affects the preconditioning response time, which indicates how long it takes for the cell to stabilize under light bias and how stable the current signal is over the entire EQE measurement. Because some perovskite solar cells have a slow change in their performance after the initial preconditioning, it is uncertain how long we should wait for the cell to stabilize. On the other hand, a long waiting time can induce cell degradation.
- One more reason that could have a possible contribution to the difference in the J_{sc} values is the strong frequency dependence of the EQE for perovskite solar cells. Therefore, an EQE measurement which involves a chopper or perturbation frequency can result a disparity in these values. This might be due to the long response time scale of the perovskite.²²

However, specialized studies would be required to elucidate and confirm the mechanism in more detail. The focus of this Viewpoint is to bring this issue to the attention of the community. Although this appears to be less relevant or reported for other PV technologies, it is noticeable for PSCs and thus should be studied in the future.

Here, we propose that the requirement for matching $J_{sc,EQE}$ and $J_{sc,JV}$ should be discussed and analyzed within the scientific community and eventually revised if needed. Currently, there is little reflection about this topic despite the empirical evidence that has been observed by many research groups thus far. Therefore, in the interest of further standardization, it is important to also look more extensively at EQE measurements and to ensure that checklists for solar cells take this into account for PSCs.

Michael Saliba  orcid.org/0000-0002-6818-9781

Lioz Etgar  orcid.org/0000-0001-6158-8520

AUTHOR INFORMATION

Complete contact information is available at:

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Notes

Views expressed in this Viewpoint are those of the authors and not necessarily the views of the ACS.

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