Standard Operating Procedure

(SOP)

Light Source Calibration

Test ID PEC-P-2

Rev 1

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Revision History

This page documents the revisions over time to the SOP. The most recent iteration should be listed in the row space, with consecutive versions following.

Date of Revision	Page(s)/Section(s) Revised	Revision Explanation
04/05/2019	All	First Release

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3. Procedures

a. Scope and Applicability – This SOP details procedures for calibrating light sources for solar equivalent (AM 1.5G or AM 1.5D) performance testing of single- and multi- junction photoelectrochemical devices. This SOP is designed for devices with optically thick semiconductor light absorber layers that conform to the idealized absorbed condition and does not cover advanced absorber concepts, molecular materials, or light management.

b. Summary of Method – Light intensity is calibrated using a reference photovoltaic (PV) cell. When a solar simulator is used or when the sample to be measured has a different bandgap or different spectral response (i.e. IPCE or EQE) than the reference PV cell, spectral corrections are applied to adjust the reference photovoltaic cell calibration current density set point. For multijunction light absorbers, the current-limiting junction is first identified by integrating IPCE over a reference spectrum, and these procedures are followed while ensuring that the current-limiting junction is also current limiting under the simulated solar spectrum (e.g. by supplementing the spectrum with LED illumination absorbed by the non-limiting junction).

c. Definitions –

- ND – Neutral density
- PV – Photovoltaic
- IPCE – Incident photon-to-current efficiency

d. Health & Safety Warning – Light sources that produce UV radiation present both acute and chronic exposure hazards to eyes and skin, and proper PPE should be worn to minimize exposure. Light sources that produce deep UV radiation (xenon) present potential ozone exposure hazards, and engineering controls must be in place to minimize exposure. Light sources that use gas-filled bulbs present explosion hazards if the bulbs overheat, and manufacturer safety guidelines must be followed to prevent injury. Arc lamps emit UV radiation, and thus can cause retinal and corneal damage if viewed directly. Long-term exposure to skin can cause burns similar to sunburn. The arc lamps require high voltage, high current power supplies which present a danger of electrical shock. Furthermore, the bulbs of the arc lamps are above atmospheric pressure when either cold or hot (2-5 atm pressure when cold and ~25 atm when in operation) and can explode during handling or normal operation. The lamp housing is strong enough to withstand a lamp envelope failure (lamp explosion). The chief hazard is during the lamp installation and removal.

e. Cautions –

- Light sources that use gas-filled bulbs present explosion hazards if the bulbs overheat, and manufacturer safety guidelines must be followed to prevent injury. Xenon lamps, which are under pressure, are operated in enclosed lamp

housings that would contain a lamp explosion should this occur. The housing also acts as a control for exposure to UV radiation. Safety glasses with UV protection side shields, standard with most current technology ocular PPE, will be worn during bulb operation. In the unusual occurrence that an operator must enter the beam for sample placement or adjustment, direct skin exposure to UV radiation from xenon light sources should be eliminated through the use of long-sleeved clothing and gloves.

- Impact-resistant safety goggles, face shield, heavy gloves, and clothing providing full skin coverage must be worn when handling new or spent lamps. Never handle a lamp while on, or soon after it has been turned off to prevent thermal burns. Don't touch bulbs with bare hands to prevent oils from causing bulb failure. Transport bulbs in protective case or original packaging and maintain original packaging for packing lamps for disposal.
- Burnt-out bulbs will be stored in the boxes they were received in, consisting of a Styrofoam encasement which guards against explosion, until disposed of according to manufacturer's guidelines.

f. Interferences – Reference PV calibrations must be accurate to ensure accurate measurement results. Light source spectra and IPCE must be accurately measured to ensure accurate spectral correction. All solar simulators have a diverging beam that is concentrated when passing through the air/glass/electrolyte interfaces of PEC cells. [3] This error is generally 10% or more for top-of-the-line commercial solar simulators, but also depends on sample area and light pathlength through the electrolyte. Underfill illumination measurements that are area-independent such as IPCE or by using an aperture are necessary to cross-validate any overfill illumination measurements.

g. Personnel Qualifications / Responsibilities – Training with laboratory safety regarding intense light sources is required. Familiarity with semiconductor light absorption physics and spectral response is needed. Familiarity with light intensity measurements is expected.

h. Equipment and Supplies –

- Light source(s) with measured spectra (Xe-based arc lamp, tungsten-halogen, ELH, or ELN, LED-based solar simulator)
- Calibrated PV reference cell
- Optical filters (high and low pass filters where $\lambda_{cut} = E_{bg}^{top}$)
- Multimeter or potentiostat
- Apparatus for adjusting light intensity (movable supports or ND filters)

i. Step by Step Procedure <u>(LIST ALL PERTINENT STEPS, IN ORDER, AND THE MATERIALS NEEDED TO ACCOMPLISH)</u>

    - Instrument or Method Calibration and Standardization – PV reference cells must be calibrated against a reference spectrum (AM 1.5G or AM 1.5D). Photocurrent from the PV reference cell should be read using a

multimeter when the PV is illuminated by the light source. Spectra of any light source(s) must be measured using a calibrated spectroradiometer across a range of wavelengths appropriate for any devices that will be tested using the light source(s) to be calibrated. Using the spectrum of the light source to be calibrated, the ratio of solar equivalent current density between the reference PV and the light absorber that will be tested must be calculated. Because the spectrum of the laboratory light sources differ from the solar reference spectrum, solar-equivalent current densities for materials of different band gaps or different spectral responses will be reached at different overall light intensities. As shown in Figure 1 using vertical dashed arrows, a tungsten source calibrated to solar equivalency (equivalent photon flux above the bandgap) for GaInP would generate 80 mA/cm^2 current for an Si photoelectrode based on integration of the lamp spectrum. This current density is 1.814 times as large as the solar (thermodynamic) limit of 44.1 mA/cm^2.

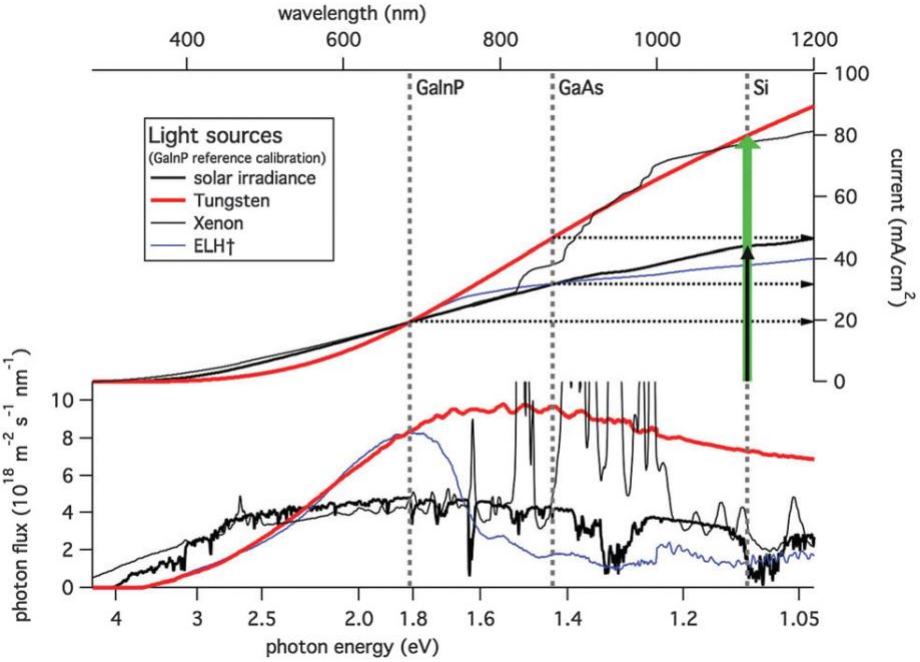


Figure 1: Current limitation vs. absorber bandgap for AM1.5 global illumination as well as for various laboratory white-light sources (top) based on reference-cell calibration exemplified for an externally calibrated GaInP reference solar cell.

- Sample Collection –
  Calibration for single absorber PEC devices
  1. Position the reference PV where the PEC device will be positioned for testing
  2. Use a multimeter to read the current of the reference PV when not illuminated (background illumination should be minimized to the point that it is negligible. Transparent electrochemical

cells are much more prone to capture/pipe ambient light than a flat PV device, which can upset the calibration)

3. Illuminate the reference PV using the light source to be calibrated and read the current
4. Subtract the dark current from the illuminated current to get the photocurrent due to illumination
5. Adjust intensity of the light source by either adjusting distance or using ND filters.
6. Repeat steps 2-5 until the photocurrent reaches solar equivalency for the device to be tested
7. Note: When it is possible to obtain the spectral response (IPCE) of the sample and reference cell as well as the spectrum of the solar simulator, a spectral correction should be calculated and applied to adjust the reference cell calibration set point.

Calibration of light sources for multiple absorber PEC devices:

1. Identify the current-limiting junction by measuring IPCE of each junction and integrating each over AM1.5G spectral flux.
2. Integrate the IPCE of each junction over the solar simulator spectral flux to make sure that the same junction will also be current limiting under the simulated spectrum. If not, supplement the simulated spectrum with LED light as appropriate.
3. Use a reference cell with a bandgap close to that of the current-limiting absorber's bandgap and perform a spectral correction calculation to adjust the reference cell calibration current set point.
4. Use a multimeter to read the current of the reference PV when not illuminated
5. Illuminate the reference PV using the light source to be calibrated and read the current
6. Subtract the dark current from the illuminated current to get the photocurrent due to illumination
7. Adjust intensity of the light source being calibrated by either adjusting distance or using ND filters
8. Repeat steps 4-7 until the photocurrent reaches solar equivalency for the appropriate absorber layer

- Sample Handling and Preservation – Not applicable for this SOP.
  - Sample Preparation and Analysis – Not applicable for this SOP.

  - Troubleshooting – Stray and scattered light can be a significant source of error for light source calibration. The reference PV should be mounted in an opaque, non-reflective housing to minimize stray light. Glassware used for PEC testing can exacerbate this issue, so

calibration should be performed with the reference PV outside of any glassware. During PEC measurements, glassware should be masked to whatever extent is possible. IPCE measurements integrated over a solar reference spectrum of PEC devices (covered elsewhere) can be used to set an upper limit for photocurrent densities expected for solar equivalent illumination. If these limits are exceeded, recalibration of light sources may be necessary.

- Data Acquisition, Calculations & Data Reduction Requirements – The spectral correction procedures are based on those used for a primary reference cell (RC) calibration, where the short-circuit photocurrent of a reference cell, measured outdoors, is translated to reference illumination (for example AM1.5D or AM1.5G). Here, the device to be benchmarked takes the place of the reference cell. The measured photocurrent I_{sc}^{meas} is translated to reference conditions by solving for the unknown cell current I_{REF}^{UN}.

$$I_{REF}^{UN} = \frac{I_{SIM}^{UN}}{M}\frac{I_{REF}^{RC}}{I_{SIM}^{RC}}$$

where I_{sc}^{0} is the desired photocurrent, E_{meas} is the total measured irradiance in W/m^2, and M is the so-called mismatch number, given by

$$M = \frac{\int_a^b E_{SIM}(\lambda)\ SR^{UN}(\lambda)d\lambda \cdot \int_a^b E_{REF}(\lambda)\ SR^{RC}(\lambda)d\lambda\ I_{SIM}^{RC}}{\int_a^b E_{REF}(\lambda)\ SR^{UN}(\lambda)\ d\lambda \cdot \int_a^b E_{SIM}(\lambda)\ SR^{RC}(\lambda)d\lambda}.$$

The CN accounts for the spectral mismatch between the measured simulated spectrum $E_{ISIM}(\lambda)$, the reference spectrum $E_{REF}(\lambda)$, and the IPCE or spectral response of the device, $SR^{RC}(\lambda)$, and as noted above is on the order of ~1% for our measurements. The integration is taken over the wavelengths 300 - 4000 nm of the full solar spectrum. In principal, $E_{meas} = \int_{300}^{4000} E_{INC}(\lambda)d\lambda$, but we use (different subscripts to distinguish between the two quantities, since in practice they are measured on separate instruments, each with its own accuracy.
For tandem devices, I_{sc}^{0} is first calculated for each junction individually using its subcell $SR^{RC}(\lambda)$, assuming that it is the current limiting junction. The quoted I_{sc}^{0} for the tandem device is then taken as the lower value between the two subcell values.

- Computer Hardware & Software – Not applicable for this SOP.

j. Data and Records Management – Not applicable for this SOP.

4. Quality Control and Quality Assurance Section

Not applicable for this SOP.

5. Reference Section

R1. ASTM G173-03(2012), Standard Tables for Reference Solar Spectral Irradiances: Direct Normal and Hemispherical on 37° Tilted Surface, ASTM International, West Conshohocken, PA, 2012, www.astm.org

R2. H. Döscher, J. L. Young, J. F. Geisz, J. A. Turner and T. G. Deutsch, *Energy Environ. Sci.* **2016**, *9*, 74-80

R3. J. L. Young, M. A. Steiner, H. Döscher, R. M. France, J. A. Turner, and T. G. Deutsch, *Nat. Energy*, **2017**, *2*, 17028

R4. C.R. Osterwald, *Solar Cells*, **1986**, *18*, 269-279