Standard Operating Procedure

(SOP)

IPCE Measurements for Tandem PEC Devices

Test ID #PEC-P-3

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

Outline/Table of Contents

1. Title Page
2. Table of Contents
3. Procedures
    a. Scope and Applicability
    b. Summary of Method
    c. Definitions
    d. Health & Safety Warning
    e. Cautions
    f. Interferences
    g. Personnel Qualifications / Responsibilities
    h. Equipment and Supplies
    i. Step by Step Procedure
        - Instrument or Method Calibration and Standardization
        - Sample Collection
        - Sample Handling and Preservation
        - Sample Preparation and Analysis
        - Troubleshooting
        - Data Acquisition, Calculations & Data Reduction Requirements
        - Computer Hardware & Software
    j. Data and Records Management
4. Quality Control and Quality Assurance Section
5. Reference Section

3. Procedures

a. Scope and Applicability – This SOP details procedures for performing IPCE measurements on single- and multi- junction photoelectrochemical devices. This SOP does not cover advanced absorber concepts, molecular materials, or devices with specialized light management. This document does not address the measurement corrections needed if luminescent coupling is present in multijunction PEC devices.

b. Summary of Method – A potentiostat is used to measure photocurrent as a function of illumination wavelength for a PEC device in contact with a solution. The measured photocurrent at each wavelength is normalized by monochromatic photon flux to give the efficiency with which photons generate current. If reaction kinetics are limiting, a comparison of measurements with and without a facile redox couple could be used. For a photoelectrode that does not split water spontaneously, the measurement may be performed with an electrical bias, which must be reported. For multijunction photoelectrodes, the total device photocurrent is that of the current-limiting junction, so "bias light" is supplied to one junction to establish the other junction as current-limiting. For the example of a GaInP/GaAs tandem, the device may be illuminated continuously with a 532-nm LED while measuring IPCE of GaAs subcell, and with a 808-nm LED while measuring the IPCE of the GaInP subcell. The flux of the LED should typically be several times that of the flux from the monochromated source to ensure that the subcell being measured is current limiting at all wavelengths. (Example: A Xe-based monochromated light source has several very large emission peaks in the IR. If corresponding features are observed in the IPCE measurement of a GaAs subcell, the bias light intensity to the GaInP subcell is not sufficiently high.)

c. Definitions –

- PEC - Photoelectrochemical
- IPCE – Incident photon-to-current efficiency
- EQE – External quantum efficiency
- WE – Working electrode
- RE – Reference electrode
- CE – Counter electrode
- BLS – Broadband light source

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 – The monochromated illumination must be well characterized to ensure accurate results. Photodiodes with NIST-traceable spectral response calibration data should be used (e.g. ThorLabs FDS100-CAL). Since all solar simulators have a diverging beam and JV measurements are generally conducted with illumination overfilling the active area, the light will be concentrated when passing through the air/glass/electrolyte interfaces of PEC cells.[1] 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. Thus, it is highly recommended that IPCE measurements are performed with a spot size smaller than the sample active area (i.e. underfill illumination) to serve as a validation measurement that is active-area independent and absent of the PEC cell concentration error.

Since the photocurrents measured during IPCE are relatively small, dark or background current should be identified and either subtracted out or a dark box/enclosure should be used.

Non-ideal photoelectrodes that exhibit transient, capacitive current should allow sufficient time at each wavelength for the photocurrent to stabilize, otherwise the IPCE data will be inflated. Typical stabilization times can be

several seconds or longer and chopping frequencies of 1 Hz or faster generally lead to error.

g. Personnel Qualifications / Responsibilities – Personnel should be familiar with standard electrochemical techniques and photoelectrochemical testing procedures.

h. Equipment and Supplies –

1. Potentiostat
2. Photoelectrochemistry cell
3. Counter electrode (typically a large area Au or Pt electrode)
4. Reference electrode
5. Broadband light source
6. Bias light source(s) – must be able deliver light to each individual subcell at a flux at least a few times greater than the monochromated BLS without providing light absorbed by the other subcell
7. Monochromator
8. Calibrated photodiode
9. Optional: Electrolyte solution containing a (non-photoabsorbing) facile redox species (commonly ferrocene/ferrocenium or derivatives) and supporting electrolyte

i. Step by Step Procedure

- Instrument or Method Calibration and Standardization – The monochromated light output must be measured at each wavelength using a photodiode of a known (calibrated) EQE. Photodiodes with measured, NIST-traceable EQE can be obtained from Thorlabs or other vendors. The monochromator should be scanned with the same step size and slit width as will be used for IPCE measurements and the photodiode response should be recorded for each step. Most lamps require about 20 minutes of operation before time-stable output is achieved.

- Sample Collection – If a redox couple is used that has absorption features overlapping that of the photoelectrode being measured, the electrolyte solution should be prepared with ≤ 1 mM total of the reduced and oxidized forms of the redox couple to minimize light absorption by the couple. The sample will be operated as the WE of the electrochemical cell and must be fully immersed in the electrolyte solution.

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

- Sample Preparation and Analysis –

1. Identify suitable potential/bias: Ideally, IPCE should be measured in a two-electrode short-circuit configuration if possible. For photoelectrodes that do not split water at short circuit, a bias may be applied during IPCE measurements by using a 3-electrode system where the potential is known. The broadband JV measurements may be used to identify a suitable potential to apply during IPCE. However, a direct translation between performance under 1-sun broadband and that of IPCE measurements is generally not expected. Since IPCE is measured at low light flux, the kinetic overpotentials are lower and thus the photocurrent onset greater. This may be explored experimentally by comparing 1-sun JV measurements to a JV measurement taking under illumination of the IPCE system. Although not typical for fairly ideal photoelectrodes, IPCE may be dependent on applied potential or have a non-linear dependence on light intensity. If such dependencies are suspected, such measurements can be informative and should be explored and reported.
2. Using the calibrated photodiode, measure the monochromatic output at each wavelength (typically step size of 10 nm) by measuring the photocurrent response of the calibrated photodiode at each wavelength. The positioning should ensure that all of the monochromatic light is focused within the photodiode active area and the photodiode should not be placed in a filled/empty beaker or any other "simulated" PEC condition. Any dark or background current should be avoided or subtracted out. The calibration data of the photodiodes is typically collected at short circuit, and these lamp calibration measurements should also be done at short circuit.
3. For tandem absorber devices, illuminate the device using bias light for the subcell for which IPCE is not being measured.
4. Measure the photoelectrode photocurrent at each illumination wavelength with any dark or background current mitigated or subtracted. The positioning should ensure that all of the monochromatic light is focused within the photoelectrode active area.

   To calculate the IPCE at each wavelength, the lamp output is assumed constant between the photocurrent measurement by the calibrated photodiode and the photoelectrode sample. With the IPCE of the calibrated photodiode known, the photoelectrode sample IPCE can be calculated by setting equal the ratio of the two IPCE/phtocurrent for each illumination wavelength

- Troubleshooting – Chopping frequencies often need to be 0.2 Hz or slower to allow any capacitive currents to settle out. Some ideal systems could be measured at slightly higher frequencies if there is no transient current.

- Data Acquisition, Calculations & Data Reduction Requirements –

IPCE as a function of wavelength can be calculated as the ratio of current measured using the PEC device divided by the current measured using the known photodiode.

- Computer Hardware & Software – Note: Ideally, measurement automation should be used (e.g. via Labview) to control both the monochromator and potentiostat throughout the wavelength sweep. Example of one step in automation sequence: Monochromator moves to first/next wavelength, shutter opens, potentiostat continuously records current, current is allowed to stabilize, a period of data points after stabilization is averaged, the shutter closes, potentiostat continues to record current, current is allowed to stabilize, a period of data points after stabilization is averaged, the difference between the stabilized current averages measured with shutter open vs closed is calculated to give the measured photocurrent at that wavelength.

- If automation is not possible with available equipment stepping the monochromator in a single step from sub-bandgap wavelengths to above bandgap wavelengths at the start of the sweep will create an instantaneous capacitance current that can be read in the i-t curve to identify the time at which the sweep began.

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

R2. J. L. Young, M. A. Steiner, H. Döscher, R. M. France, J. A. Turner, and T. G. Deutsch, *Nat. Energy*, **2017**, *2*, 17028