Standard Operating Procedure

(SOP)

Measurement of Product Crossover and Faradaic Efficiency

Test ID #PEC-P-5

Rev 1

Prepared By: Todd Deutsch, Burton Simpson, James Young	Date
Approved By: Chengxiang Xiang	Date
Approved By: NAME / TITLE	Date

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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 performing Faradaic efficiency measurements on photoelectrochemical devices. This SOP is intended for use to measure these quantities for direct solar water splitting devices, but the general principles may be adapted for other systems

b. Summary of Method –This measurement determines the fraction of current measured in the PEC circuit that is consumed in the water reduction and oxidation half-reactions, a quantity known as Faradaic efficiency (FE).

c. Definitions –

- FE – Faradaic efficiency
- MS – Mass spectrometry
- J-V – Current density –voltage

d. Health & Safety Warning – Hydrogen gas is flammable. The work area should be thoroughly ventilated and free from and any sources of ignition during these tests.

e. Cautions – Not applicable for this SOP.

f. Interferences – For the Hoffman apparatus, temperature fluctuations can introduce error, so temperature should be recorded at the time of measurement. Ambient pressure also influences the measurement and should be reported, but its variation is expected to be less under normal circumstances.

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

h. Equipment and Supplies –

1. Potentiostat
2. Photoelectrochemical device
3. Photoelectrochemistry cell
4. 2x Pt electrodes
5. Broadband light source
6. Calibrated light source (SOP available)
7. Electrolyte solution
8. Hoffman apparatus
9. Capillary mass Spectrometer

i. Step by Step Procedure

- Instrument or Method Calibration and Standardization – Prior to measurement, both instruments should be calibrated for known quantities of gas. This is best achieved by using H_2 and O_2 calibration gas source and delivering a known quantity of gas using calibrated flow controllers/meters. A suitable alternative is to perform *in situ* electrolysis of water with the platinum electrodes in the same photoelectrochemical cell setup. This should be performed in a two-electrode configuration with one Pt electrode as the anode and the other as the cathode. Fixed amounts of charge should be passed at multiple current densities relevant to the expected device performance (e.g. 10 mA/cm^2 with a 1 cm^2 electrode for 10 minutes to produce 6 mC).

- Sample Collection –

  Temperature should be measured with a thermometer and atmospheric pressure should be measured with a barometer at the time of volume measurement for the Hoffman apparatus

  Capillary MS: The photoelectrochemical cell must be thoroughly sparged with ultrahigh purity inert (carrier) gas for at least 20 minutes prior to starting each measurement. For capillary MS, the response for O_2 and H_2 should be monitored during this period until stable baselines are established.

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

- Sample Preparation and Analysis –

  Hoffman Apparatus
  1. Illuminate the PEC device with the calibrated light source for a fixed amount of time while recording photocurrent or cumulative charge passed
  2. Read the volume change due to gas evolution once all bubbles have reached the headspace.

  Capillary Mass Spectrometry
  1. Thoroughly sparge the cell with Ar until stable H_2 and O_2 ion current background/baselines are reached
  2. Illuminate the PEC device with the calibrated light source for a fixed amount of time while recording photocurrent or cumulative charge passed
  3. Record the H_2, O_2, N_2, and Ar ion currents during operation

- Troubleshooting – N_2 and Ar currents are read during measurement for the purpose of leak detection. Increases in N_2 current that correlate with decreases in Ar current may indicate leaks.
- Data Acquisition, Calculations & Data Reduction Requirements –

  Hoffman Apparatus:

  1. Calculate moles of gas produced using the ideal gas law:

$$moles = \frac{P_g V}{RT}$$

  Where P_g is the pressure contribution from the evolved gas alone. V is the volume measured on the Hoffman apparatus. R is the gas constant (0.08206 (L*atm/K*mol)) and T is temperature in Kelvin.

  2. P_g is the adjusted gas pressure inside the measurement chamber which takes into account only contributions from the evolved gases. Calculate P_g using the formula

$$P_g = P_{atm} - P_{H2O} + P_{elec}$$

  Where P_{atm} is atmospheric pressure, P_{H2O} is water vapor pressure, and P_{elec} is the electrolyte pressure.
  3. Measure P_{atm} with a barometer at the time of measurement.
  4. Record the temperature at the time of volume measurement and look up P_{H2O} in physical reference handbooks
  5. Measure the difference in height (Δh) in mm between the central reservoir and the gas/electrolyte boundary. Calculate P_{elec} using the formula

$$P_{elec} = \Delta h \times \frac{\rho_{Hg}}{\rho_{elec}} \times \frac{1\ atm}{760\ mmHg}$$

  6. Calculate Faradaic efficiency using the formula

$$\eta_F = \frac{moles}{t}\frac{nF}{I}$$

  Where n is the number of electrons passed per reaction, F is Faraday's constant, t is the collection time, and I is the operating current density of the PEC device

  Capillary Mass Spectrometry

  1. Subtract the baseline ion currents for H_2 and O_2 from the ion current data for calibration and sample measurements.
  2. Plot the average ion current for H_2 and O_2 for the last 10 seconds of each calibration measurement against the current density for that point
  3. Use linear regression to find the calibration curve
  4. Convert ion current in the sample measurements to equivalent current density

STH Efficiency

1. Obtain J_{SC} from J-V measurements using a calibrated light source (See Light Sources SOP)
2. Calculate solar-to-hydrogen efficiency using the formula

$$\eta_{STH} = \frac{|J_{SC}|\left(\frac{mA}{cm^2}\right) \times 1.23\ (V) \times \eta_F}{P_{total}\left(\frac{mW}{cm^2}\right)}$$

Where J_{SC} is the short-circuit current density and P_{total} is the total irradiance.

- 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. 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