Standard Operating Procedure

(SOP)

Spatially Resolved PEC Activity by Scanning Electrochemical Microscopy

Test ID PEC-P-18

Prepared By: Burton Simpson	Date
Approved By: Chengxiang Xiang	Date
Approved By: NAME / TITLE	Date

Date: 11/02/2021

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

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

The following are topics that may be appropriate for inclusion in technical SOPs. Not all will apply to every procedure or work process being detailed. If a particular topic does not apply, leave the topic heading in and insert "Not applicable for this SOP".

a. Scope and Applicability – This SOP details procedures for mapping the the photoelectrochemical activity of photoelectrodes by SECM. This SOP details methods to characterize photocatalytic activity on either n-type photoanodes or p-type photocathodes. This method is applicable to planar electrodes with low aspect ratio surface structures.

b. Summary of Method – A collection mode SECM image is taken of the illuminated photoelectrode in aqueous media to quantify the rate of either hydrogen or oxygen evolved during catalysis.

c. Definitions – SECM – Scanning Electrochemical Microscopy
UME – Ultramicroelectrode, the electrode on the probe in SECM
a – UME radius
d – tip- substrate separation
L – tip-substrate separation divided by the UME radius
RG – ratio of the glass radius surrounding the UME to the UME radius
Substrate – The surface being analyzed by SECM
i_{tip} – Tip current
i_{ss} – Diffusion limited tip current
i_s – Subtrate current
HER – Hydrogen evolution reaction
OER – Oxygen evolution reaction
HOR – Hydrogen oxidation reaction
ORR – Oxygen reduction reaction

d. Health & Safety Warning – Ultraviolet light can be damaging to skin and eyes. Appropriate measures to avoid exposure such as enclosure or ultraviolet blocking PPE should be utilized.

e. Cautions – Care must be taken to avoid damaging SECM tips after preparation, as deviations in tip geometry from ideal cases may lead to unreliable results. If using an Hg/Au alloy tip for ORR measurements, as suggested below, the tip must be biased to a potential negative of the Hg/Hg^{2+} formal potential at all times when in solution to avoid corrosion of the Hg.

f. Interferences – Care must be taken in selecting tip material to ensure that only the desired PEC product is being detected. As oxygen is present in the atmosphere, it is recommended that collection of oxygen from photoanodes is

performed in an inert atmosphere such as a flush box. If one is not available, care must be taken to ensure that the SECM cell can be thoroughly sparged.

g. Personnel Qualifications / Responsibilities – Personnel should be thoroughly familiar with electrochemistry, electrochemical instrumentation, and should be thoroughly trained in SECM operation.

h. Equipment and Supplies –

- Photoelectrode
- SECM
- SECM cell
- UME probe (Pt for H_2 collection, Au/Hg for O_2 collection)
- Reference electrode
- Counter electrode
- Electrolyte solution
- Outer sphere redox species (optional, for approach curve)

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 –
  Approach curve and alignment (perform w/ oxygen prior to sparging, or use an outer sphere redox species)
  1. Position the UME close to the surface by eye
  2. Bias the tip at a potential at which the i_{ss} is reached for oxygen or the outer sphere redox species
  3. Perform an approach curve where the tip moves slowly enough for the tip to reach steady state at each step. During this approach, the tip should be unbiased and in the dark.
  4. Stop the approach when $i_{tip} = 0.7i_{ss}$. This typically puts the tip at a distance of ~1 tip radius from the surface, if the tip is experiencing negative feedback during the approach.
  5. Determine the tip size using the equation shown in the Calculations section
  6. Using the tip size, fit the RG using the method referenced in the Caclulations section.
  7. Several approach curves should be performed across the surface to ensure that the substrate plane is aligned normal to the z-axis of the SECM. See the instrument's instructions for correcting any tilt of the sample relative to the SECM.

- Sample Collection – Not applicable for this SOP.

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

- Sample Preparation and Analysis –

1. Sparge the solution in the SECM cell thoroughly with an inert gas prior to imaging
2. Position the UME at a height of 1L above the surface
3. Perform an image of the substrate with the substrate illuminated (and biased, if necessary)to perform either the HER or OER. The tip should be biased to perform the reverse reaction (HOR or ORR, respectively). The tip should be stepped in the x and y directions an amount approximately the size of the tip. The rate of movement should be similar to that used in the approach curve.
4. Approximate collection efficiencies can be determined using R3, which can be used to approximate local HER or OER current from i_{tip}, as discussed in the Data Acquisition, Calculations & Data Reduction Requirements Section.

- Troubleshooting – Significant drift in in tip current may occur if images take a long time to acquire. This can often be due to accumulation of product gasses over long periods of time. It is recommended that short acquisitions are used with adequate sparging in between.

- Data Acquisition, Calculations & Data Reduction Requirements –

  Tip size can be calculated using the following equation:
  $i_{ss}=4nFaDc^*$
  Where n is the number of electrons transferred for each molecule electrolyzed at the tip, F is Faraday's constant (96485 C/mol), D is the diffusion coefficient of the species being electrolyzed, and c^* is the bulk concentration of the species being electrolyzed.

  The RG of the tip can be calculated by fitting approach curve data to equation 26 in R2 as follows:
  1. Make a spreadsheet that includes a column for the fixed values a and i_{ss}, as well as values of RG and L_{end} that can be varied (10 is recommended as a starting value for RG and 1 for L_{end}). L_{end}
  2. Create a column using your data representing the tip-substrate separation normalized by tip radius: $L = d/a+L_{end}$. If the approach curve recorded distance starting at z = 0 and increasing as the tip approached the surface, $d = z_{end}-z$
  3. Create a column from your data representing tip current normalized by the steady state current at infinite distance: $I = i_{tip}/i_{ss}$
  4. Make a column calculating the approach curve as a function of L and RG using equation 26:

$$I(L,RG) = \left[\frac{2.08}{RG^{0.358}}\left(L - \frac{0.145}{RG}\right) + 1.585\right] \times \left[\frac{2.08}{RG^{0.358}}(L + 0.0023RG) + 1.57 + \frac{ln(RG)}{L} + \frac{2}{\pi RG} ln\left(1 + \frac{\pi RG}{2L}\right)\right]^{-1}$$

5. Adjust RG and L_{end} until the calculated and real curves match

Collection efficiency can be reasonably approximated for tip electrodes with a ~ 12.5 and RG 6-10 or 25 µm and RG 3-6 using equations 9 and 10, respectively, in R3. Tip that vary significantly from these geometries should use finite element simulation similar to what was performed in R3 using COMSOL to determine accurate collection efficiencies. These simulations assume local homogeneity on a scale of 50-100 µm, denoted as *b*, so results will be approximate for features smaller than this scale.

1. Calculate the CE for the tip size using either equation 9 (12.5 µm) or equation 10 (25 µm)

Equation 9: $CE^{max} = A + B\left(\frac{d}{a/b}\right) + C\left(\frac{d}{a/b}\right)^2 + D\left(\frac{d}{a/b}\right)^3 + E\left(\frac{d}{a/b}\right)^4$

Equation 10: $CE^{max} = A + B\left(\frac{d}{a/b}\right) + C\left(\frac{d}{a/b}\right)^2 + D\left(\frac{d}{a/b}\right)^3$

Where the values for A, B, C, D, and E, can be taken from the tables below:

Table 1. Empirical Parameter Values and Correlation Coefficient (R^2) for Equation 9 with $a = 12.5\ \mu m$, RG = 6−10, and $b = 50\ \mu m$

RG	*A*	*B*	*C*	*D*	*E*	R^2
6	103.38	−2.1681	0.02585	-1.485×10^{-4}	3.22×10^{-7}	0.9998
10	104.07	−1.641	0.01574	-7.85×10^{-5}	1.57×10^{-7}	0.9998

Table 2. Empirical Parameter Values and Correlation Coefficient (R^2) for Equation 10 with $a = 25\ \mu m$, RG = 3−6, and $b = 50\ \mu m$

RG	*A*	*B*	*C*	*D*	R^2
3	101.01	−1.6114	0.01583	-6.43×10^{-5}	0.9994
6	102.17	−1.1589	0.00814	-2.64×10^{-5}	0.9997

2. Convert i_{tip}(x,y) to i_{sub}(x,y) using the equation

$$i_{sub} = \frac{i_{tip}}{CE(L)}$$

3. Plot an image of i_{sub}

- Computer Hardware & Software – Calculations of tip size and RG can be performed using a spreadsheet software such as Excel. For best accuracy of collection efficiency, numerical simulations with a finite

element simulation such as COMSOL is needed. A computer is needed to control the potentiostat and motor controller of the SECM.

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

4. Quality Control and Quality Assurance Section

Not Applicable to this SOP

5. Reference Section

R1. Bard, A. J.; Faulkner, L. R., *Electrochemical methods : fundamentals and applications*. 2nd ed.; Wiley: New York, 2001; p xxi, 833 p.

R2. Lefrou, C., Cornut, R. *ChemPhysChem,* **2010**, *11*, 547–556.

R3. Sánchez-Sánchez, C. M., Rodríguez-López, J., Bard, A. J. *Anal. Chem.* **2008**, *90*, 3254-3260