Standard Operating Procedure

(SOP)

Determination of HER and OER Activities for Water Splitting

Test ID # PEC-P-13

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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

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3. Procedures

a. Scope and Applicability – This SOP details procedures for determining the activity and stability of catalysts for the hydrogen and oxygen evolution reactions

b. Summary of Method – XPS is used to determine the working catalyst's elemental composition. Cyclic voltammetry is used to determine the electrochemically active surface area of the catalyst. Rotating disk voltammetry, potential steps, and/or current steps are used to determine the catalytic activity of the catalyst. Finally, a controlled current electrolysis is performed to estimate the temporal stability of the catalyst. Optionally, controlled current electrolysis may also be used to determine the Faradaic Efficiency of the catalyst or to perform extended stability tests.

c. Definitions – HER – Hydrogen evolution reaction
OER – Oxygen evolution reaction
XPS – X-ray photoelectron spectroscopy
ECSA – Electrochemically active surface area
CV – Cyclic voltammetry
RDE – Rotating disk electrode
η – Overpotential
i_c – Charging current
v – Scan rate
C_{DL} – Double layer capacitance
C_S – Specific capacitance
j_s – Specific current density (using ECSA instead of geometric area)
FE – Faradaic efficiency, the fraction of charge passed that was used to create the desired product

d. Health & Safety Warning – Hydrogen gas is flammable. The work area should be thoroughly ventilated and free from any sources of ignition during these tests. Strongly basic or acidic electrolyte solutions can be corrosive and appropriate safety precautions, such as safety glasses and gloves, should be taken when working with these.

e. Cautions – Some catalysts may degrade especially rapidly at the potentials or current densities suggested in this protocol. Appropriate ranges should be chosen.

f. Interferences – Not applicable for this SOP

g. Personnel Qualifications / Responsibilities – Familiarity with electrochemical measurement techniques.

h. Equipment and Supplies –

1. Potentiostat
2. 2-chamber electrochemistry cell that separates the working electrode from the counter and reference electrodes
3. Counter electrode
    a. Cathode - typically a large area carbon electrode or boron doped diamond, as small amounts of dissolved platinum or gold can change the activity of catalysts
    b. Anode – IrO_x/Ir (RuO_x is not stable)
4. Reference electrode (mercury-based reference electrodes such as Hg/Hg_2SO_4,Hg/HgO, and SCE are preferred due to silver electroplating from Ag/AgCl reference electrodes)
   *Ag/AgCl electrodes has larger drift of potential over time, whereas $Hg/HgSO_4$ and Hg/HgO are much more stable over time.

5. Electrolyte solution containing supporting electrolyte appropriate for the catalyst
6. For faradaic efficiency: O_2 or H_2 probe for OER or HER, respectively

i. Step by Step Procedure

- Instrument or Method Calibration and Standardization – This protocol may be performed using a catalyst of well characterized activity (e.g. Pt for HER) to ensure the reproducibility of measurements

- Sample Collection – Not applicable for this SOP.

- Sample Handling and Preservation –
    1. Never touch the front surface of the semiconductor, especially with bare hands.

- Sample Preparation and Analysis – Prepare electrodes for RDE measurements.

- Troubleshooting – Not applicable for this SOP.

- Data Acquisition, Calculations & Data Reduction Requirements –

  Elemental Composition by XPS
    1. Collect a survey spectrum of the catalyst
    2. Collect high resolution spectra of the component elements
    3. Fit XPS data to extract the number of gaussian components, the binding energies and widths, and infer the chemical speciation in combination with knowledge of the elemental composition.

  ECSA

1. Set up the electrochemical cell in a three-electrode configuration with the catalyst electrode as the working electrode
2. Purge the electrolyte solution with the product gas (O_2 for OER, H_2 for HER) for 30 minutes
3. In a quiescent solution, perform CVs to determine a non-Faradaic potential range (typically a 0.1 V window around OCP)
4. All current within the non-Faradaic range should be due to i_c, from which C_{DL} can be determined using the equation $i_c = \nu C_{DL}$
5. Determine ECSA using the equation $ECSA = \frac{C_{DL}}{C_S}$
6. Divide ECSA by the geometric area of the electrode to determine the roughness factor of the electrode

Catalytic Activity by RDE

1. Set up the electrochemical cell in a three-electrode configuration with the catalyst electrode as the working electrode on the RDE
2. Purge the electrolyte solution with the product gas (O_2 for OER, H_2 for HER) for 30 minutes
3. Rotate the RDE at 1600 rpm for all measurements
4. Perform a CV using a 0.01 V s^{-1} scan rate going from OCP to at least 10 mA cm^{-2}
5. Perform 30 s controlled current chronopotentiometric steps stepping from 0.1 to 20 mA cm^{-2} (using 1, 2, and 5 at each decade) to determine the initial overpotential required for these currents
6. Perform 30 s controlled potential chronoamperometric steps stepping η from 0 to 0.6 V in 0.05 V steps to determine j_s at these potentials

Stability Measurements (Time at specific Current Densities)

1. Use the electrochemical setup for which the Catalytic Activity Setup by RDE steps have already been performed. Ideally, These experiments should use fresh electrodes for which no electrochemical pretreatment has been performed.
2. Perform a 2 hr controlled current chronopotentiometric step at 10 mA cm^{-2} (and at each current density, 100 mA cm^{-2}, etc.)
3. Repeat the ECSA and Catalytic Activity by RDE procedure
4. Repeat step 2 using a 22 hr step, then repeat step 3
5. Repeat the Elemental Composition by XPS procedure
6. Report overpotentials and specific current densities at 0, 2, and 24 hours of operation
7. Perform ICP-OES/ICP-MS – Taking a small quantity of electrolyte every 2-4hr to check the dissolution of catalyst during stability measurements

Faradaic Efficiency

1. Set up the electrochemical cell in a three-electrode configuration with the catalyst electrode as the working electrode on the RDE.

Alternatively, use a sealed, two-compartment, three-electrode cell connected to a GC auto-sampler.

2. Measure the product gas concentration with the probe in air
3. Purge the electrolyte solution with the product gas (O_2 for OER, H_2 for HER) for 30 minutes. Stop purging, then measure the product gas concentration with the probe
4. Purge the electrolyte solution with inert gas (N_2 or Ar) for 30 minutes. Stop purging, then measure the product gas concentration with the probe
5. Rotate the RDE at 1600 rpm and perform a 15 min controlled current chronopotentiometric step at 10 mA cm^{-2}
6. Stop rotation, and measure the product gas concentration with the probe
7. Calculate the dissolved concentration of gas produced using the three point calibration (air, saturated, inert)
8. Convert this concentration to the amount produced by multiplying by solution volume. Convert to total charge using Faraday's constant (96485 C/mol).
9. Divide this by the charge passed by the electrode to get FE

- Computer Hardware & Software – Computers for XPS and potentiostat control. CasaXPS or equivalent for fitting of XPS data. Data analysis software capable of performing basic mathematical operations.

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

4. Quality Control and Quality Assurance Section

5. Reference Section

R1) C. L. C. McCrory, S. Jung, I. M. Ferrer, S. M. Chatman, J. C. Peters, and T. F. Jaramillo. *J. Am. Chem. Soc.* **2015**, *137*, 4347-4357