Standard Operating Procedure

(SOP)

3-Electrode Cell for Screening

OER/HER Electrocatalyst Activity

LTE-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
7/13/2021	All	Initial Release

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1. Title Page

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3. Procedures

a. Scope and Applicability – method for screening HER/OER electrocatalysts using fully immersed electrodes covered with electrocatalyst. Optimized for usage in alkaline solutions with high loading of electrocatalysts up to 4 mg/cm^2. Can be used for both PGM and PGM-free catalysts.

b. Summary of Method – This procedure describes a 3-electrode electrochemical test of catalysts for use as water splitting (OER/HER) materials.

c. Definitions:
DI – de-ionized water
SOP – Standard Operation Procedure
SHE – Standard Hydrogen Electrode
HER – Hydrogen Evolution Reaction
OER – Oxygen Evolution Reaction
PGM – Platinum Group Metals

d. Health & Safety Warning – Do not touch the electrochemical cell, wires, or potentiostat while the experiments is in progress to prevent electrical shock. Be aware of all hazards listed in the SDS for the electrolyte used in the electrochemical cell.

e. Cautions – Do not allow any electrodes or exposed wires to touch while an electrochemical measurement is running. Always store reference electrodes in the standard solution appropriate for the reference type. Do not allow reference electrode to dry out.

f. Interferences – not observed.

g. Personnel Qualifications / Responsibilities – Following proper safety training on the electrical equipment used in this protocol, these experiments can be done by technicians, undergraduate students, graduate students, and postdoctoral researchers.

h. Equipment and Supplies –

- Electrode of interest
- Pt wire
- Standard reference electrode (Hg/HgO for 0.1 or 1M KOH)
- DI water
- Electrolyte solution
- Potentiostat
- Inert gas and sparging tube

- Multimeter (optional)
- A second, new and unused reference electrode of the same type as the first (optional)

i. Step by Step Procedure:

- Instrument or Method Calibration and Standardization – Ensure that the reference electrode is in working order by checking it against a fresh, unused reference electrode OR by preparing a hydrogen reference electrode using one of the following two procedures:
    1. Fresh reference: Immerse the reference electrode and another fresh, unused reference electrode of the same type into an electrolyte solution. Use a multimeter to measure the potential between the electrical leads on the two reference electrodes. The magnitude of the difference should be <5 mV for the reference to pass the calibration check.
    2. Hydrogen electrode: Assemble a 3-electrode cell with a platinum working electrode, any compatible counter electrode, the desired reference electrode, and an acidic electrolyte with a 1 M proton concentration ($[H^+]$). Run a cyclic voltammogram (CV) in which the current switches from cathodic to anodic (or vice versa). The potential corresponding to 0 current should be ± 5 mV from the theoretical potential of the reference electrode versus the standard hydrogen electrode (SHE).

- Sample Collection – Prepare the 3-electrode cell and perform electrochemical measurements on the working electrode according to the steps below.
    1. Turn on the potentiostat and software. Ensure that the potentiostat is communicating with the software.
    2. Rinse the electrochemical cell, electrodes, and inert gas feed tube with DI water.
    3. Prepare electrolyte solution with the desired salt concentration.
    4. Add electrolyte solution to the electrochemical cell.
    5. Sparge the electrolyte with N_2 gas for at least 10 minutes before starting an electrochemical experiment and continue to bubble gas through the electrolyte during electrochemical measurements.
    6. Add electrodes to the cell and connect them to the appropriate leads on the potentiostat. Use the water splitting catalyst (either OER or HER) as the working electrode, a Pt wire as the counter electrode (in case of PGM catalysts) or graphite rod (in case of PGM-free catalysts), and an Hg/HgO reference electrode. Make sure that none of the electrodes are in contact with each other above, or while submerged in, the electrolyte. Make sure that none of the alligator clips used to mount the

electrodes are in contact with the electrolyte. Measure the geometric area of the working electrode that is exposed to electrolyte (recommended to use 1x1cm).

7. For OER catalysts, condition the catalyst for testing by performing a CV between 0.5 and 1 V vs. SHE at 50 mV/s for 50 cycles. For HER catalysts, condition the catalyst for testing by performing a CV between 0 and -0.5 V vs SHE at 50 mV/s for 50 cycles.
8. For OER catalysts, perform a pre-hold OER performance test by performing a CV between 1.2 and 2.1 V vs SHE at 10 mV/s once. For HER catalysts, perform a pre-hold performance test by performing a CV between 0 and -0.5 V vs SHE at 10 mV/s once.
9. Perform bulk electrolysis by performing chronopotentiometry. Hold at 0 A for 3 s for the induction period followed by 20 mA for 1 h for the electrolysis period, and end with 0 A for 1 s in the relaxation period.
10. For OER catalysts, perform a post-hold performance test by running a CV between 1.2 and 2.1 V vs SHE at 10 mV/s once. For HER catalysts, perform a post-hold performance test by running a CV between 0 and -0.5V vs SHE at 10 mV/s once.
11. Turn off the inert gas flow.

- Sample Handling and Preservation – Rinse electrodes and electrochemical cell in DI water and allow to air dry after electrochemical testing.

- Sample Preparation and Analysis – Use 1.5x1cm stainless steel mesh. Put it into pure ethanol and sonicate on ultrasonic bath for 10 minutes. Dry in air for 15 minutes. Deposit calculated amount of ink on the surface of mesh using a spray method. (Take note if other deposition methods are used to ensure repeatability among samples). Dry at 50C for 25 minutes. Measure the weight of coated electrode to ensure correct loading of electrocatalyst (i.e., 1, 2 or 3 mg/cm^2)

- Troubleshooting – main issues with 3-electrode method are related to poor electric contact between wires connected at the working electrode, reference electrode, counter electrode and the connection to the computer. These should be checked before starting the experiment.

- Data Acquisition, Calculations & Data Reduction Requirements – Divide the current measured during the experiments by the surface area of the working electrode to calculate current density.

- Computer Hardware & Software – standard laptop or desktop with corresponding potentiostat connection (at 2021 are available in USB and wireless connections). Software is supplied with potentiostat (Biologic, Pine Instruments or other vendors).

j. Data and Records Management – collected polarization curves can be used for calculation of either current density at required potential or potential at operational current density (i.e. 0.2 A/cm^2 @ 1.8V).

4. Quality Control and Quality Assurance Section

It is required to repeat each working electrode at least two times. In case of the difference in current density more than 10%, repeat for a 3rd trial in order to find the relevant data.

5. Reference Section

E. Creel, et al, Front. Energy Res., 26 May 2022, Sec. Process and Energy Systems Engineering Volume 10 - 2022 https://doi.org/10.3389/fenrg.2022.871604