

# **Standard Operating Procedure (SOP)**

## **ROTATING DISK ELECTRODE**

**Test ID # LTE-P-10**

**Rev 3**

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### 1. Procedures

a. Scope and Applicability – This protocol is written for the standardization of rotating disk electrode experiments for the ex-situ characterization of oxygen evolution reaction catalysts for PEM water electrolyzers. This protocol should allow for the analysis of onset potential, overpotential at a fixed current, catalytic activity, and electrochemical surface area of these catalysts.

b. Summary of Method – This protocol describes the preparation and execution of rotating disk electrode experiments including:

- Preparation of the electrolyte solution
- Preparation of the catalyst ink
- Setup of the electrochemical cell and its components
- Drying of the catalyst film on the disk electrode
- Setup of the rotating disk electrode shaft
- Execution of the rotating disk electrode electrochemical tests

c. Definitions –

- RDE – Rotating Disk Electrode
- OER – Oxygen Evolution Reaction

- PEM – Proton Exchange Membrane
  - ECSA – Electrochemical Surface Area
- d. Health & Safety Warning –
- Chemical Hazards – This test protocol uses concentrated acids for the preparation of the electrolyte and the cleaning of the glassware. When handling the concentrated perchloric acid or sulfuric acid solutions, be sure to follow all safety precautions utilized in the SDS. All concentrated acids should be handled in a fume hood and if using concentrated perchloric acid, be sure to use a fume hood that is approved for perchloric acid use. Standard personal protective equipment, including safety glasses and gloves (compatible with acids used), must be worn at all times. Ensure that all gas cylinders being used in the experiments are properly secured and regulated.
  - Rotation Hazard – The RDE shaft may be rotating during some tests to as high as 2500 RPM. Be sure to keep your body, hair, or clothing away from the shaft as it is rotating.
- e. Cautions –
- One major source of error with RDE is contamination. Ensure that all glassware and every component of the RDE process is clean prior to starting RDE tests.
  - When affixing the RDE tip to the rotating shaft, be sure to hold the shaft in place (while the rotator is off) and tighten the RDE tip. Turning the RDE shaft in order to set the RDE tip could damage the rotator.
- f. Interferences –
- There is a potential for signal noise to interfere with the electrochemical measurements. To minimize issues with signal noise, all metal objects near the electrochemical cell should be properly grounded. One common technique would be to connect any metal objects, such as clamps, to the earth ground connection on the front panel of the RDE control unit.
- g. Personnel Qualifications / Responsibilities –
- All personnel should be trained to handle chemicals and to mitigate chemical hazards
- h. Equipment and Supplies –
- All equipment is suggested but not required. Comparable capabilities should be sought in any alternatives.
    - Personal Protective Equipment
      - Safety Glasses
      - Gloves
      - Lab Coat
    - Glassware
      - 1 L Volumetric Flask
      - Beakers (2 – 50 mL and 1 – 1 L)
      - 20 mL vials

- RDE Electrochemical Cell (Pine Research: AKCELL3)
- Gas Inlet Bubbler (Pine Research: RRP086)
- Equipment
  - Electrode Rotator (Pine Research: AFMSRCE)
  - Rotating Disk Electrode Tip (Pine Research: AFE5TQ050)
  - RDE Working Electrode – Gold Disk (Pine Research: AFED050P040AU)
  - Silver Chloride Reference Electrode (Pine Research: RREF0021)
  - DHE reference electrode preferred to reduce contamination sources, [http://www.gaskatel.de/eng/produkte/hydroflex/eng\\_hydroflex\\_index.html](http://www.gaskatel.de/eng/produkte/hydroflex/eng_hydroflex_index.html)  
*This type of reference electrode is preferred.*
  - Platinum or Gold wire and mesh counter electrode (ex: Pine Research: AFECTR5). *Gold is preferred.*
  - Electrode Polishing Kit (Pine Research: AKPOLISH)
  - Potentiostat (BioLogic SP-240 or other)
  - Micropipettes and Disposable Tips (10 – 100  $\mu$ L and 100 – 1000  $\mu$ L)
  - Bath Sonicator
  - Parafilm
- Chemicals
  - Perchloric Acid (70%, Veritas® Double Distilled, GFS Chemicals: 230)
  - Sulfuric Acid (ACS Reagent, 95-98%, sigma Aldrich: 258105)
  - Inert gas, Nitrogen or Argon (Ex: Airgas: AR UHP 300)
  - Deionized Water (Mili-Q Miliopore quality minimum standard)
  - Isopropanol (Certified ACS, Fisher Scientific: A416)
  - Nafion® Dispersion, 1100EW at 5 wt% (Fuel Cell Store: D521)
  - Iridium Oxide (Alfa Aesar: A17849)
  - ALNOCHROMIX™ Solution (Alconox Inc.)

i. Step by Step Procedure

- Instrument or Method Calibration and Standardization –
  - Ag/Ag/Cl Reference (per Pine Research Reference Electrode Product Guide):
    - Keep an extra reference electrode (same as the electrode to be checked) properly stored.
    - Submerge both the reference electrode to be checked and the extra reference electrode in the filling solution
    - Use a voltmeter to check the potential difference between the electrodes. If the potential difference is greater than 5 mV, the reference electrode that is being checked should be discarded or refreshed.
      - To refresh the reference electrode:
        - Replace the internal filling solution of the electrode with deionized water for 24 hours
        - Replace the internal filling solution of the electrode with deionized water and soak the frit

of the electrode in deionized water at 80°C for 1 hour.

- Dip the frit in distilled water and sonicate for 10 minutes
- *Dynamic Hydrogen Reference is preferred to prevent contamination over long duration tests per Alia et al.*
- Sample Collection –
  1. Any glassware or vessels, components etc. that are used in the preparation of electrolyte or electrochemical testing must be first cleaned according to the following procedure:
    - To thoroughly clean all glassware and electrochemical cell, use the following procedure written in Shinozaki et al:
      - Soak all glassware in concentrated sulfuric acid overnight.
      - Soak all glassware in ALNOCHROMIX™ solution overnight
      - Immerse the electrochemical cell in deionized water and boil the water in the cell
      - After the water boils, remove the water and refill and repeat the deionized water rinse and boil procedure up to 8 times.
      - Rinse the electrochemical cell with 0.1 M perchloric acid solution 2-3 times.
    - Following the conclusion of each test, ensure that all glassware, all cell that have previously been cleaned are placed in an adequately sized and cleaned glass beaker and filled with deionized water. Cover the beaker with a watch glass to prevent contamination and evaporation. Periodically this beaker and cell must be recleaned.
  2. 0.1M Perchloric Acid Electrolyte Preparation
    1. Fill a clean 1 L volumetric flask about 2/3 full with deionized water.
    2. Weigh 14.39 g of concentrated perchloric acid into a clean beaker and add the perchloric acid into the volumetric flask.
    3. Rinse the beaker that contained the perchloric acid multiple times with deionized water and pour the diluted perchloric acid into the volumetric flask until the solution is nearly to the 1 L mark. Slowly fill the volumetric flask to the 1 L mark.
    4. Mix and invert the flask to ensure that the electrolyte solution is homogeneously mixed.
  3. Rinsing and Setup of the RDE Configuration
    1. Boil the water in the beaker that the cell is in. Let stand until cooled or handle with care and appropriate heat resistant gloves. Rinse cell components with DI water carefully (2-3 times), taking care to not to touch the inside surfaces of the cell or other parts that will be in contact with electrolyte. Place cell at test stand.

2. Fill the electrochemical cell approximately  $\frac{1}{2}$  to  $\frac{3}{4}$  full with the electrolyte solution. Swirl the electrolyte in the cell prior to emptying the solution in the proper waste container. Repeat this step at least twice.
3. Fill the electrochemical cell with the electrolyte solution so that the reference electrode, gas bubbler and counter electrode are all submerged in the electrolyte solution and not in contact with each other. If there are any unused ports on the electrochemical cell, cover the ports with cleaned glass or PTFE stoppers. Record volume of solution for effluent analysis purposes.
4. Remove the reference electrode from the storage solution bottle and rinse the electrode thoroughly with deionized water. Insert the reference electrode into the electrochemical cell.
5. Rinse the inlet gas bubbler with deionized water multiple times until clean. Rinse the gas bubbler thoroughly with deionized water one final time before inserting the gas bubbler into the electrochemical cell.
6. Remove the counter electrode from the fritted glass tube or the cell holder beaker. Rinse the counter electrode with deionized water. Reassemble the counter electrode and insert it into the electrochemical cell.
  1. CAUTION: The counter electrode is fragile. Be cautious when handling the counter electrode to avoid breaking the wire or wire/mesh bonds.
  2. Best practice is to have a higher surface area counter electrode, enabled with the use of a mesh spot welded to a lead wire.
  3. Au counter electrodes are preferred over Pt since upon dissolution they will not activate the OER. Dissolution will occur over long term tests per Alia et al. The use of a carbon counter electrode could introduce other sources of contamination.

#### 4. Preparing, Polishing, and Assembling the RDE Tip

1. Fixed working electrode tips are preferred over ChangeTips. PTFE shrouds are preferred (for room temperature only). Au tips are encouraged over glassy carbon, for long term testing Au is required.
2. If using an AFT5EQ ChangeTip RDE working electrode from Pine Research, use the ChangeDisk Toolkit (Pine Research: AFE6K050) to remove the gold disk from the RDE tip. Ensure no electrolyte leakage occurs. Evaluate leakage and contamination with time. CAUTION: Be cautious to avoid scratching the surface of the gold disk. There is a small spring in the U-cup assembly of the RDE tip which could cause the disk to be ejected and scratched.

3. Polish the RDE tip with Electrode Polishing Kit (Pine Research: AKPOLISH) or equivalent.
4. For standard cleaning, affix a microfiber polishing cloth from the kit to a flat, still surface. Place a small amount of 0.05  $\mu\text{m}$  polishing slurry onto the microfiber cloth. In a Figure-8 pattern, polish the gold disk for about 4 minutes. Sonicate in deionized water for 3x3 minutes, replacing the deionized water between each step to ensure the removal of leftover alumina polishing paste. Rinse the disk thoroughly with deionized water when polishing is completed.
5. Dry with compressed nitrogen gun or air dry with protective beaker covering the surface of the tip.

#### 5. Preparation and Application of the Catalyst Ink

For catalyst ink and electrode preparation, use the following procedure written in Alia et al<sup>7</sup>:

1. Using a small, clean spatula, measure 3.5 mg of Iridium Oxide into a clean vial. Once the correct amount of iridium oxide is in the vial, cap the vial to prevent contamination.
2. Using a 100 – 1000  $\mu\text{L}$  micropipette, dispense a total of 7.6 mL of deionized water into vial.
3. After replacing the tip of the micropipette, use the micropipette to dispense a total of 2.4 mL of 2-propanol into vial.
4. Use a clean 10 – 100  $\mu\text{L}$  micropipette to dispense 40  $\mu\text{L}$  of Nafion® dispersion (1100EW at 5 wt%) into the catalyst ink. Tightly cap the vial. Note: Depending on type of material, the Nafion content may have to be altered for optimal properties.
5. Sonicate the ink for 20 minutes and add Nafion afterwards. Sonicate only for 1 - 2 minutes after adding Nafion in a sonication bath. Validate dispersion of the ink by observing if there is catalyst settling. One example protocol is the following.  
Using a bath sonicator:
  - a) Use an ice bath or cooled solution to prevent overheating of the ink
  - b) Sonicate the catalyst ink in an ice bath for 20 minutes.
6. Place the RDE tip and rod into the rotator upside down so that the ink can be drop cast on the RDE tip.
7. Once sonicated, use the micropipette to dispense a 10  $\mu\text{L}$  drop of catalyst ink onto the gold disk of the working electrode that is set to a 100 rpm rotation rate. Turn up the rotator slowly from 100 RPM to 700RPM. Wait until dry (~15 minutes) before turning off the rotation. Once the film is dry, place a drop of the electrolyte solution on the thin film to prevent contamination.
  - a) NOTE: The drop of catalyst ink should not come in contact with the PTFE shroud of the RDE



tip. The drop should only dry on the surface of the gold disk. There should not be any bubbles in the droplet once it is added to the gold disk. After drying, the ink should be uniform, and no coffee-ring effects should be observed. If any of these issues are noticed, it is best to remove the droplet and repeat.

#### 6. Preparation of the RDE for Testing

1. For temperature control during testing, jacketed cells could be used if cleanliness of the experiment and cell can be maintained. Otherwise rely on room HVAC systems is preferred.
2. Connect an inert gas cylinder with the gas bubbler. Slowly increase the regulator pressure from the cylinder until gas begins bubbling in the electrochemical cell. The gas should purge through the electrochemical cell for at least 15 minutes prior to beginning electrochemical measurements.
  1. CAUTION: If the regulator pressure is set to high initially, electrolyte solution could be sprayed out of the electrochemical cell. Slowly meter the flow of the gas until it just begins to bubble.
  2. Ar is preferred since it could be more inert than N<sub>2</sub>. In either case, UHP grade is recommended.
3. Remove any protective cover from the working electrode and insert the working electrode into the electrolyte solution.
4. Using the potentiostat, attach the appropriate cables to the working electrode port, reference electrode, and counter electrode.

NOTE: With many RDE setups, the connections to the working electrode could be placed into 4 different ports. Typically, two of those ports are used for RDE while the other two ports are used for RRDE (Rotating Ring Disk Electrode) experiments. Refer to the manual of the equipment being used to ensure that the potentiostat is connected to the RDE plug.

#### 7. Electrochemical Testing

- 1) Electrochemical measurements may begin once the electrochemical cell has been purged with inert gas, the potentiostat is on and connected to the RDE setup, and the RDE tip is immersed in the electrolyte.
- 2) Compensation of experiments during testing. It is preferred to actively compensate for solution resistance using the potentiostat. Depending on the potentiostat, perform the solution resistance compensation prior to Cyclic Voltammetry (CV), activity measurements. The resistance can also be removed

during post processing but could result in overcorrection and inflation of the kinetic performance of individual samples. Do not compensate durability tests.

- 3) Cyclic voltammogram measurements:
  - a) The purpose of this discrete test is to characterize the fingerprint of the Ir in a potential range that is outside of water splitting. The Ir-oxide may partially reduce under these conditions.
  - b) If potentiostat allows, immerse the RDE tip at 1.2 V (vs RHE). Otherwise immerse under closed or open circuit voltage conditions.
  - c) Break-in the film by performing cyclic voltammetry where the voltage is cycled between 0.025 V and 1.5 V vs. RHE at a rate of 500 mV/s for 50 cycles.
  - d) Following the conditioning step, record cyclic voltammetry where the voltage is cycled between 0.025 V and 1.0 V vs. RHE at a rate of 20 mV/s (and/or 50 mV/s) for at least 2 cycle. If CV is consistent this is an adequate fingerprint of the material. If the CV is not consistent in the first 2 cycles, more are needed to get an adequate fingerprint.
  - e) We note that testing OER subsequently could alter OER performance as a result of surface reduction of the oxide.
- 4) Oxygen evolution reaction activity measurements
  - a) The purpose of this discrete test is to evaluate the OER activity of the electrocatalyst.
  - b) If potentiostat allows, immerse the RDE tip at 1.2 V (vs RHE). Otherwise immerse under closed or open circuit voltage conditions.
  - c) Run conditioning 50 cycles, 1.2–1.8 V at 100 mV/s. with a rotation rate of 2500 RPM.
  - d) Next using the same potential window reduce the scan rate to 20 mV/sec to collect activity data. Scan from 1.2 to “n” V. Take activity value at “n”, where n is 1.55, 1.65 and 2 V, taken in separate experiments on fresh materials.
  - e) The potential of comparison (1.55, 1.65, 2 V) may need to be changed based on catalyst loading and intrinsic activity. In any case, Tafel plots should be consulted to ensure that activities were compared at a potential where the observed current was within the kinetic region and not biased by capacitance.
- 5) Durability test
  - a) The purpose of this test is to assess the short-term durability of the electrocatalyst under aqueous testing conditions (test results should not be used for predicting long term durability). The upper voltage limit and time should be

chosen based on the purpose of the test. Note do not compensate for solution resistance during durability tests:

- i) Activity screening: In this case short term measurements are taken over a fixed interval. For instance, 1.55, 1.65 or 2.0 V to coincide with activity measurement in step 4. This testing should be performed over fixed timeframes ranging from minutes to hours depending on the availability of instrumentation and sensitivity of effluent analysis. 1 hr is recommended.
  - ii) Durability translation for MEA testing: In this case a longer-term test is performed at high voltage to replicate MEA type conditions. Following the cyclic voltammetry and activity measurements, test the stability of the catalyst at 2.0V vs. RHE over 13.5 hrs per Alia et al.
  - iii) Following the conclusion of the stability test withdraw the RDE tip, preferably prior to allowing the surface of Ir to reduce below 1.2V. Stir solution to ensure mixing, then carefully pour or pipette 10 mL of solution into a aliquoting vessel for ICP-MS. Replicates and repeated tests are encouraged. Three samples per test condition is suggested.
  - iv) To reassess activity after durability testing, use fresh solution and repeat step 4 (OER Activity).
- Sample Handling and Preservation –
    - If there is any significant time between the drying of the thin film and the start of any testing, cover the RDE tip without introducing any organic contaminants, ensure that nothing touches the thin film prior to or during testing.
    - If there is a brief amount of time between the drying of the film and the start of the testing, place a small drop of deionized water or electrolyte solution on the thin film to prevent contamination from the air.
    - If there are any open ports to the electrochemical cell, ensure that the electrolyte solution does not get contaminated by covering any port with either a stopper or Parafilm. Ensure that the electrolyte does not touch any foreign material (gasket or parafilm, or PTFE stoppers other than those cleaned according to the same procedures outlined above).
    - Following the conclusion of each test, ensure that all glassware, all cell that have previously been cleaned are placed in an adequately sized and cleaned glass beaker and filled with deionized water. Cover the beaker with a watch glass to prevent contamination and evaporation. Periodically this beaker and cell must be recleaned.
    - To check for the presence of catalyst material in the electrolyte (catalyst degradation): Stir solution to ensure mixing, then carefully pour or pipette 10 mL of solution into a aliquoting vessel for ICP-MS. Record

the volume/mass of cell with and without electrolyte at the starting point of the test.

- Sample Preparation and Analysis –
    - See “Sample Collection” above
  - Troubleshooting –
    - If the activity of the standard catalyst is much lower than expected, there could be an issue with cleanliness. To thoroughly clean all glassware, use the cleaning process described in section i.
  - Data Acquisition, Calculations & Data Reduction Requirements –
    - Onset Potential
    - ECSA
    - Catalytic Activity (see section d, step 4)
  - Computer Hardware & Software –
    - The potentiostat software will be required to perform the electrochemical tests and may be able to assist in data analysis. This software may be hardware specific and not standardized for this protocol.
- j. Data and Records Management –
- TBD
2. Quality Control and Quality Assurance Section
- Check RDE Cleanliness with Polycrystalline Pt or Ir Disk
    - Looking for reproducibility of the cyclic voltammogram of a freshly polished Pt or Ir disk without signs of cation, anion adsorbates or organic contaminants
3. General Notes

When evaluating catalysts for the oxygen evolution reaction in acidic or alkaline electrolytes, polycrystalline gold electrodes are typically used as the working electrode substrate, due to a combination of the relatively low activity, high oxidation potential, and slow dissolution rate. The use of gold, however, can result in oxide growth that can electronically isolate portions of the catalyst layer; or dissolution that can delaminate the catalyst layer. Ink and coating process optimization is necessary to minimize substrate/electrolyte contact and substrate contributions to catalyst durability measurements, along with limiting the operating potential and avoiding internal resistance corrections. [10,11] Gold as a substrate also impacts surface area measurements and duplicate experiments with glassy carbon electrodes may be necessary for surface area validation. [12] Although the counter electrode choice is less critical in oxygen evolution due to the operating potential, gold may be necessary under circumstances where negative current is applied to condition the working electrode.

When evaluating catalysts for the hydrogen evolution reaction in alkaline electrolytes, glassy carbon is typically used as the working substrate due to the low potential. Gold is typically used as the counter electrode due to the low activity compared to other platinum group metals, and to avoid contaminant effects from dissolved carbon counters that can lower activity measurements and shorten cell use. [13] Gold, however, can dissolve and plate the working electrode, and limiting current density and using high surface area counters is necessary to minimize the impact. [13]

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