Standard Operating Procedure

(SOP)

Defining ASR for SOEC Devices

Test ID: HTE-P-19

Tyler Hafen, Joseph Hartvigsen 3/4/2021

Prepared By: NAME / TITLE Date

Approved By: NAME / TITLE Date

Approved By: NAME / TITLE Date

Date: mm/dd/yyyy

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

1. Procedures

    a. Scope and Applicability

        i. The purpose of this procedure is to establish a common method for calculating ASR (area specific resistance) for a SOEC device.

    b. Summary of Method

        i. Using current and voltage data from an electrolysis I-V sweep to calculate the apparent ASR and the intrinsic ASR using mathematical formulas.

    c. Definitions

        i. SOEC – Solid Oxide Electrolysis Cell
        ii. ASR – Area Specific Resistance – Internal resistance of a SOEC stack normalized for area ($A*cm^2$).
        iii. Apparent ASR – That resistance obtained from the slope of the IV curve of current density (current/active area of the cell) and cell voltage (individual or Stack Voltage/#cells)
        iv. Intrinsic ASR – The resistance based on incremental changes that take in to account the localized Nernst potential at each point ($A*cm^2$).
        v. HTE - High Temperature Electrolysis

    d. Health & Safety Warnings

        i. One should conduct their own Hazardous Operations Review to ensure they are practicing safe operations for their facility.
        ii. Some potential hazards:
            1. Steam (pressure hazards and burns)
            2. Electrical Shock (high voltage and current)
            3. Burns from hot surfaces

    e. Cautions

        i. Insure proper polarity connection of the power supply or Potentiostat / Galvanostat to the SOEC device.
        ii. Shut down or disconnection of the power source equipment must be done properly to avoid damage to the SOEC device.

f. Interferences

    i. Measurement equipment should be calibrated in its HTE test location to account for any electrical interferences.

g. Personnel Qualifications / Responsibilities

    i. Familiarity in the use of math and algebra
    ii. Electrochemical testing and good lab practices

h. Equipment and Supplies

    i. Potentiostat / Galvanostat for single cells and or DC power supply and current shunt for stacks
    ii. Data collection & analysis software to record voltage/current values and to produce IV plots for a SOEC stack or single cell.
    iii. DC power supply, shunt, voltmeter
    iv. Instrument or Method Calibration and Standardization
        1. The potentiosat /galvanostat used to record IV characteristics should be regularly calibrated with a standard to insure accurate measurements.
        2. The calibration method will depend on the particular device, but values should be calibrated in the range of actual measurements expected from the SOEC device and while in the normal test location
        3. Calibrate according to manufacturer specifications

i. Step by Step Procedure

    i. Define or calculate needed values:
        1. Expected minimum and maximum for current or voltage
        2. Steps desired for IV sweeps
        3. Active area of the cell(s)
        4. Number of cells in a stack
        5. Gas feed rates
        6. Stack/cell operating temperature & pressure

    ii. IV Sweep & Calculate the Apparent ASR:
        1. Sweep the cell or stack using either current or voltage steps. Record both the current and voltage reading at distinct points from OCV to the desired operating condition. Using a graphing program (e.g. Excel) plot the IV characteristics of the single cell or stack in the form of cell voltage (y-axis) vs. current density (x-axis).
        2. The current density can be calculated by dividing the current at any point by the active area of the cell.

3. For a stack the cell voltage can be calculated by dividing the stack operating voltage at each point by the number of cells in the stack. For single cell test you can use the voltage values taken during the sweep.
4. Plot a best fit line through the data and calculate the slope of the line. The apparent ASR will be equal to the slope of the line.

iii. Calculate the Intrinsic ASR**:**

1. "Apparent" ASR [$R_a^{"} = \left(\frac{V_{op}-V_{OC}}{j_i}\right)$] does not address flow variations or observed activation polarization.
2. So, we define an "Intrinsic" ASR as
   a. $R_i^{"} = \left(\frac{V_{op}-\overline{E_N}-V_{add}}{j_i}\right)$
3. With an additional offset voltage V_{add}, which has been determined to be approx. 0.003 V for co-electrolysis and 0.03 V for dry CO_2 electrolysis (0 for steam).
4. The integral average H_2O reduction Nernst potential is defined as:

$$\overline{E_N} = \frac{\int_{[H_2]_{inlet}}^{[H_2]_{exit}} \Delta G_{H_2O}\, d[H_2]}{2\mathcal{F}([H_2]_{exit} - [H_2]_{inlet})}$$

   i. $\Delta G_{H_2O}([H_2]) = \Delta G^{\circ}(T) + RT \ln\left(\frac{[H_2]\sqrt{[O_2]}}{(1-[H_2])}\right)$
   ii. $[H_2O] = 1 - [H_2]$

   b. Which evaluates and simplifies as:

$$\overline{E_N} = \frac{\left([H_2]_{exit}\Delta G_{H_2O}([H_2]_{exit}) - [H_2]_{inlet}\Delta G_{H_2O}([H_2]_{inlet}) + RT \ln\frac{([H_2]_{exit}-1)}{([H_2]_{inlet}-1)}\right)}{2\mathcal{F}([H_2]_{exit} - [H_2]_{inlet})}$$

5. The above equations assume steam electrolysis operation. If performing CO_2 electrolysis, the equations still apply by replacing H_2/H_2O with CO/CO_2.
6. If performing co-electrolysis, then the water gas shift reaction at a given temperature must be accounted for:
   a. Water-gas shift: $CO + H_2O <-> CO_2 + H_2$
   b. Equilibrium composition:
      i. $pH_2 = pH_2 + x$
      ii. $pCO_2 = pCO_2 + x$
      iii. $pCO = pCO - x$
      iv. $pH_2O = pH_2O - x$
   c. $K_p = \frac{(pCO2+x)(pH2+x)}{(pCO-x)(pH2O-x)}$

7. Fit *iASR* temperature variation:
    a. $f(T) = Ae^{\left(\frac{-E_{act}}{RT}\right)}$
        i. Such that $f(1073°K) = 1$

iv. Computer Hardware & Software

1. Data acquisition hardware and software to record current and voltage measurements at specific times as well as gas flows and stack temperature.

j. Data and Records Management
    i. IV data and calculated results should be recorded and saved in a secure location and backed up in a physically separate location.

2. Quality Control and Quality Assurance Section

a. QC activities are designed to allow self-verification of the quality and consistency of the work. Describe the preparation of appropriate QC procedures (self-checks, such as calibrations, recounting, re-identification) and QC material (such as blanks – rinsate, trip, field, or method; replicates; split samples; spikes; and performance evaluation samples) that are required to demonstrate successful performance of the method. Specific criteria for each should be included. Describe the frequency of required calibration and QC checks and discuss the rationale for decisions. Describe the limits/criteria for QC data/results and actions required when QC data exceed QC limits or appear in the warning zone (control charts). Describe the procedures for reporting QC data and results.

3. Reference Section

a. Documents or procedures that interface with the SOP should be fully referenced (including version number), such as they relate to the SOP, published literature, or methods manuals. Citations cannot substitute for the description of the method being followed in the organization. Attach any that are not readily available. References should be numbered (1, 2, 3, … etc.) and may be used as a footnote. Use an acceptable format for citing a reference (see examples provided below).

b. R1. 40 CFR 30, Code of Federal Regulations, "Grants and Agreements With Institutions of Higher Education, Hospitals, and Other Non-Profit Organizations."

c. R2. ANSI/ASQC E4-1994, *Specifications and Guidelines for Quality Systems for Environmental Data Collection and*

Environmental Technology Programs, American National Standard, January 1995.

d. R3. U. S. Environmental Protection Agency, 2000a. *Guidance for Data Quality Assessment: Practical Methods for Data Analysis (QA/G-9)*, EPA/600/R-96/084, Office of Environmental Information.