# Standard Operating Procedure

# (SOP)

# Determination of Ionic Transference Numbers: Electromotive Force (e.m.f.) Method

## Test ID: HTE-P-02

## Rev 1

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| Ani Kulkarni / Senior Scientist | 03-25-2019 |
| Prepared By: NAME / TITLE | Date |
| Approved By: NAME / TITLE | Date |
| Approved By: NAME / TITLE | Date |

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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 |
|---|---|---|
| 04/15/2019 | All | First Release |
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3. **Procedures**

**a. Scope and Applicability** – The purpose of this SOP is to describe a method for evaluation of ionic transference number in mixed ionic electronic conductor ceramics intended for use in solid oxide electrolysis or solid oxide fuel cells. In this method, different partial pressures of gas ($H_2$ or $O_2$) are maintained over the two sides of ion conductor solid oxide membrane (typically a disc). In the modest approximation, an ionic transference number ($T_i$) is the ratio between the measured voltage and the Nernst voltage. A number of different partial pressure combinations are averaged to obtain $T_i$.

**b. Summary of Method** – A prefabricated electrolyte disc is used with two circular electrodes on both sides fabricated by screen printing the disc with Pt paste and subsequent heat treatment. The two electrodes are hermetically isolated from each other using appropriate sealing (glass, gold or ceramic in a test fixture. The test fixture could be same as a button cell test fixture for SOEC. A precision gas mixer (Okolab - Tri-gas mixer, MIX-2000 Digital or equivalent) is used to supply gas mixtures and to accurately control the partial pressures of gases on electrodes. The voltage (emf) across the sample is measured over the range of partial pressure and temperatures to determine ionic transference number using a high precision multi-meter (e.g. Keithley 2002 Series or equivalent). The background voltage is measured without a gradient.

**c. Definitions** –solid oxide electrolysis cell (SOEC); hydrogen ($H_2$); platinum (Pt); open circuit voltage (OCV), electromotive force (emf), oxygen partial pressure ($P_{O2}$)

**d. Health & Safety Warning** – Only trained personnel should operate the test rig and cell fabrication equipment. Appropriate safety measures for remediation of the hazards and risks associated with powders and solvents, electrical equipment, hot surfaces of the furnace, and flammable /asphyxiant gases should be applied. Refer to safe working instructions, personal protective equipment guidelines, HSE practices and compliance requirements in your lab.

**e. Cautions** – Hot surfaces, flammable/asphyxiant gases, hazardous chemicals.

**f. Interferences** – Any electromagnetic interference associated due to main power supply, a stray voltage due to furnace windings and Seeback effect.

**g. Personnel Qualifications / Responsibilities** – The experiment requires basic skills in ceramic processing, dry-pressing, high-temperature sintering, use of electrical devices like DC power supply and multi-meter along with gas safety training.

**h. Equipment and Supplies** – Pre-Fabricated Solid Oxide Electrolyte Disc (1 mm thick, 18-20 mm diameter, Pt Paste, Button cell test fixture (see example in *Appendix*), Sealing material (Gold, Ceramic or glass), High impedance precision digital multi-meter, gas mixer (*MIX-2000 Digital or in-house equivalent*), a pair of hydrogen /oxygen sensors to measure the partial pressure of the gases and check sealing, Bronkhorst Steam generator-gas mixer or separate humidifier. All gases used should be of at least high purity grade.

**i.** Step by Step Procedure <u>(LIST ALL PERTINENT STEPS, IN ORDER, AND THE MATERIALS NEEDED TO ACCOMPLISH)</u>

1. An electrolyte disc is prepared by die pressing electrolyte powder into a circular disc sintered at an appropriate sintering temperatures to achieve theoretical density of more than 95% as determined by *Archimedes methods*. The suggested disc dimeter is 18 mm. On sintered disc, two Pt electrodes (8 mm dia) are screen printed using Pt ink (Engelhard 6082) on each side, and heat treated at 800°C for 1 hr to burn out the organic matter.

2. *In house* made button cell test fixture or a commercial fixture with alumina base and alumina gas tubes can be used to test the button cell. Such fixture should have arrangement for pressing spring loaded Pt meshes on the cells to make firm cell connections.

3. Before start, check the test rig for mechanical integrity of the alumina tube, test fixture and thermocouple positioning.

4. Either glass, ceramic, or gold can be used for cell sealing. Depending upon the type of sealing used (glass, gold or ceramic) and the method of seal formation (*in-situ or pre-formed*), the appropriate seal application procedures and heating/cooling cycles must be followed. (*See **Appendix** for the typical cycles for each seal type*).

5. Oxygen sensors should be connected at the outlet of both chambers to measure oxygen partial pressure (*Ideally sensors should be located close to electrodes, however, such a placement is difficult for typical button cell fixtures*).

6. Air can be used as a purge gas during seal formation. Once the sealing procedure is completed, the cell should be cooled/heated to the target temperature (3°C/min), and about 30 minutes of equilibrium time should be allowed at the target temperature.

7. Caution: $N_2$ should be used to flush the air out prior to hydrogen injection.

8. The hydrogen should be introduced on the sealed side using a constant flow rate measurable on the digital flow meter, ideally 20 ml per minute to pressure test the seal. After closing the exhaust, hydrogen flow rate should be dropped to zero. After 30 minutes, OCV should reach above 1.1 V. Based upon pressure test and OCV, seal formation can be confirmed.

9. Once the seal is formed both chambers can be flushed with a gas mixture, for example, for Proton transport number determination, both chamber can be flushed with 45% $H_2$/50% Ar /5% $H_2O$ (by volume) on both sides Such a mixture can be generated using gas mixers in combination with a *Bronkhorst* steam generator or humidifier with a heated gas line. Allow 30 minutes for equilibrium. Typical flow rates are 20 ml per minute of gas mix. (For oxygen transport number determination, number of different gas mixes including $CO_2$/CO mix can be used). The partial pressures in each chamber should also be confirmed using gas sensors at the outlet of each chamber.

10. After 30 minutes, ideally OCV should be zero. Any deviation from zero voltage, should be noted. This voltage is due to stray effects in the system and should be subtracted from any subsequent voltage measurement. It is termed as a *compensation voltage*.

11. Once *compensation voltage* is determined, partial pressure in one chamber should be varied keeping the gas composition of other mixture constant at 45% $H_2$/50% Ar / 5% $H_2O$.

12. At least 4 to 5 different partial pressures should be used, and at each partial pressure 30 minutes of equilibrium time should be allowed (or until a stable voltage value is obtained).

13. At least three different temperatures should be used, and step 8 and 9 should be repeated.

14. The data can be logged using a Labview interface connected to flow meters, gas sensors, and DMM, or simply recorded in a lab book.

15. The transference number is given by the ratio of obtained voltage and theoretical voltage. Read references [1, 2].

- **Troubleshooting –**
  In the event of unusual results, check the gas flows and system temperature, and reset the electrochemical data acquisition system.

  If a seal leak is suspected after step 6 the in-situ heat treatment cycle should be repeated.

- **Data Acquisition, Calculations & Data Reduction Requirements –**

Data is acquired using electrochemical work station or Digital Multimeter and Labview. Most modern equipment has OEM provided software for data monitoring, control, and collection.
Reportable from the test:

- Details of test fixture (ceramic/metallic, use code for type used).
- Full details of the fabricated SOEC electrolyte disc.
- Voltage at various partial pressures and temperature.

- **Computer Hardware & Software** – OEM provided software.

j. **Data and Records Management –**

All data should be backed up as a text file as well as in format readable by software. Process conditions and time should also be noted in a Lab book.

## 4. Quality Control and Quality Assurance Section

Calibrate electrochemical work station using manufacturer provided test circuits.

Thermocouple readouts, and flow meters should also be periodically tested using manufacturer recommended procedures.

Repeated experiments are required to confirm the quality of the data.

## 5. Reference Section


1. Truls Norby, EMF method determination of conductivity contributions from protons and other foreign ions in oxides, Solid State Ionics, Volumes 28–30, Part 2, 1988, Pages 1586-1591, ISSN 0167-2738, https://doi.org/10.1016/0167-2738(88)90424-9.
2. Proton Conductive Ceramic Materials For An Intermediate Temperature Proton Exchange Fuel Cell, Jasna Jankovic, Thesis collection The University Of British Columbia. (available online)

## Appendix

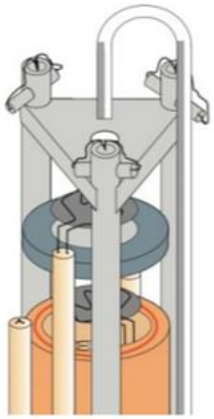


Figure: Schematic of commercial Test Fixture from NORSEC
(https://www.norecs.com/index.php?page=ProboStat)

Sealing procedure for glass and gold seals are as below:

I. For glass sealing: Glass sealing may be formed in-situ or pre-formed externally:

(a) For in-situ glass sealing, a glass ring or a paste of Schott G018-311 glass may be used. Such seals are commercially available from Schott. A typical heating cycle is: 100°C/0.5 h (5°C/min), 180°C/0.2 h (3°C/min), 720°C/1h (10°C/min) used to reach the operating temperature of the cells. During sealing either air or argon atmosphere may be used for purging the fixture. If sealing paste is desired, a glass powder may be mixed with organic binder (Ferro Corporation/Schott).

(b) For pre-formed glass seal: The glass seal is applied using glass powder slurry prepared with commercial materials such as Schott GM31107 glass powder mixed with organic binder in 4:1 wt% followed by annealing to obtain a gas tight seal (refer to instruction provided by Schott for pre-formed seal).

II. Alternatively, ceramic sealant such as Ceramabond® (Aremco) can be used, and the procedure provided by the manufacturer may be followed for pre-formed ceramic sealing.

III. Gold paste or gold rings can be used for sealing, which involves heating the cell close to the melting temperature of gold (1050°C) using a 2°C/min ramp rate, and holding at 1050°C for 20 minutes, and cooling to operating temperature (2°C/min). The ramp rates and hold time are indicative and may change with fixture design and flow rates of gases.