Standard Operating Procedure

(SOP)

Determination of Ionic Transference Numbers using Four Probe Method

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Rev 1

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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 measurement of ionic and electronic conductivity in mixed ionic electronic conductor ceramics for intended use in solid oxide electrolysis cells or solid oxide fuel cells. The method is based upon the relationship between concertation of charge carriers (ions, electrons or holes) and oxygen partial pressure of the atmosphere around the specimen. The method applies to measurement of oxygen conductivity based upon certain assumptions. For protonic conductors refer to SOP of **electromotive force (e.m.f.) method/blocking electrode method**.

b. Summary of Method – Prefabricated bar shaped specimen of the electrolyte with 95% of theoretical density is used. Four electrodes are coated on the sample using Pt paste and connected to Pt wires, and then the sample is placed in a furnace chamber (tube) equipped with a calibrated zirconia oxygen sensor. The gas mixer (*Okolab - Tri-gas mixer, MIX-2000 Digital* or equivalent) is used to supply gas mixtures to accurately control the oxygen partial pressures in the furnace chamber. CO/CO_2 or Ar/O_2 mixtures can be used. Instead of CO/CO_2 mixtures, other gas mixtures can be used including $H_2/Ar/H_2O$ mixtures to discriminate proton conduction.

c. Definitions –solid oxide electrolysis cell (SOEC); platinum (Pt); open circuit voltage (OCV), Oxygen partial pressure (P_{O2}), Digital multimeter (DMM)

d. Health & Safety Warning –Only trained persons should operate the test rig and specimen preparation chemical/equipment. Appropriate safety measures for remediation of hazards and risks associated with powders and solvents, electrical equipment, hot surfaces, and flammable (Hydrogen /Carbon Monoxide (CO)) /asphyxiant gases are mandatory. Refer to safe working instructions, personal protective equipment guidelines, best HSE practices and compliance requirements in your lab.

Special safety precautions must be observed as CO is a toxic gas (hazardous chemical) and inhalation of concentrations of only 4000 ppm in air could prove fatal in less than one hour. The Safety Data Sheet must be referred to prior to use.

All sensors should be checked for current calibration. Gas safety interlocks must be fully operational. Confirm the LED indicators/or any other indicator on the gas safety panel before use (refer to manual).

e. Cautions –. Special gas safety precautions must be observed as CO is a toxic gas (hazardous chemical).

Other precautions: Hot surfaces, flammable/asphyxiant gases, hazardous chemicals.

f. Interferences –Any electromagnetic interference associated with the main power supply, induction due to lead wires and furnace windings should be compensated for using a "dummy cell". The dummy cell could be a platinum foil or single crystal YSZ with sputtered Pt electrodes.

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

h. Equipment and Supplies – Pre-Fabricated conductivity bar, Pt paste (Engelhard 6082), Pt wires, Spring loaded high temperature test fixture, *Zahner Im6E* electrochemical test station controlled by software OR Keithley current source and Keithley precision multimeter, Test Rig with temperature controlled furnace and enclosure with gas extraction.

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

1. Before start, check the test rig for mechanical integrity of the quartz tube, test fixture and thermocouples positioning. Ensure the sealing of the quartz tube from ambient air by pressure testing at 0.5 bars with nitrogen.

2. The samples for 4-probe conductivity measurements are typically 20 to 30 mm long rectangular bars with square flat faces.

3. The two end faces of the bars should be ground flat, cleaned and painted with platinum paste (*6082 or Johnson Matthey Metal Ltd. N758*), and fired at 800°C to burn off binder material

4. The probes for measuring the potential drop should be constructed by cutting with a diamond saw a groove of ~0.25 mm wide, ~0.2 mm deep and ~ 7 mm away from each end, and wedging a 0.25 mm diameter platinum wire into each groove. 1 mm thick voltage tapping strips should be painted around the Pt wire using Pt paste. Masking tapes can be used to maintain the shape and thickness of the voltage leads. The Pt wires should be connected to the voltage measurement wires of the fixture.

5. For passing the current, spring loaded square Pt meshes should firmly contact the end faces of the bar after it is placed inside the fixture. A

number of fixture designs are available for such tests including commercial fixtures (e.g. *ProboStat – NORECS*).

6. The loaded fixture should be placed in the quartz tube with sealed ends and an oxygen sensor. The voltage lead should be connected to the DMM and the current leads should be connected to current source.

7. Typically, 3 temperatures from 600 to 800°C can be used along with various oxygen partial pressures. Minimal equilibrium time of 30 minutes is warranted at each oxygen partial pressure.

8. A constant current of 0.5 mA to 10 mA (depending upon the specimen resistance) should be supplied by a Keithley constant current source, and voltage should be recorded using a software interface connected to the DMM. Alternatively, any modern potentiostat such as *Zahner Im6E* electrochemical test station can be used for both supplying current as well as for measuring voltage.

9. Starting with air atmosphere, measure the voltages at particular current for various oxygen partial pressures. Do not exceed or go below the predicted decomposition $P_{O2.}$

10. The conductivity can be calculated using formula:

$$R = \frac{\rho l}{A}$$

ρ = Resistivity
l = Length
A = Cross section area

11. The measurement should be doublets: measure the conductivity while decreasing P_{O2} and also while 'going back' to ambient air to observe any hysteresis.

12. Plot *Log conductivity Vs* P_{O2} : For a typical ionic conductor, the electronic conductivity is proportional to $P_{O2.}$ Using defect chemistry equations, the values of ionic and electronic conductivity can be separated and the transference number can be determined. Refer to the references 1 and 2.

13. It should be noted that the method relies on certain assumptions to "separate" ionic and electronic conductivity. For more accurate separation, the electromotive force (e.m.f.) method or blocking electrode method is recommended.

- **Troubleshooting –**

Oxygen sensor must be calibrated over the range of partial pressures in a separate experiment to determine the sensor drift and deviation.

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

Insulating material can be used to avoid short circuiting the Pt wires. Unusual resistance readings may be attributed to a bad sample, broken sample and a wire, or short circuit, etc.

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

  Data is acquired using electrochemical work station or software interface for the DMM and constant current source. Most modern potentiostats have OEM provided software for data monitoring, control, and collection.

  1. Reportable from the test:

  - Oxygen partial pressure, conductivity values

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

j. Data and Records Management –All data should be backed up as a text file as well as in a format readable by software. Process conditions along with timing should be noted in a Lab book. The readouts from gas flow meters and furnace temperature controller can be integrated into the electrochemical measurement using LabVIEW software/or an Excel macro.

4. Quality Control and Quality Assurance Section

Calibrate electrochemical equipment 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.

Refer to Reference 3 for error sources and remediation.

5. Reference Section

1. Riess, Mixed ionic–electronic conductors—material properties and applications, Solid State Ionics, Volume 157, Issues 1–4, 2003,Pages 1-17,ISSN 0167-2738, https://doi.org/10.1016/S0167-2738(02)00182-0.

2. Kosacki, H.L. Tuller, Mixed conductivity in SrCe0.95Yb0.05O3 protonic conductors, Solid State Ionics,Volume 80, Issues 3–4,1995,Pages 223-229,ISSN 0167-2738, https://doi.org/10.1016/0167-2738(95)00142-S.
3. Yadunath singh, electrical resistivity measurements: a review, International Journal of Modern Physics: Conference SeriesVol. 22, pp. 745-756 (2013) H-MiscellaneousOpen Access