A method is discussed, which allows the investigation of the oxygen transport across compressed ceramic samples. In this method, coulometric titration was used to monitor the oxide ion transport upon passage of current across the ceramic samples. The oxide ion transference number was determined from the ratio between oxide ion transport and the total current. The method feasibility was tested using cerium gadolinium oxide. Subsequently, lanthanum strontium manganites were used as model materials, and their transference number was related to the oxygen diffusion coefficient through the Nernst-Einstein relation. The diffusion coefficient found by coulometric titration was compared to values found by thermogravimetry on powdered and compressed samples.

Oxygen transport kinetics

A key parameter for high performance fuel cells is an optimal three phase electrode structure with a high number of active sites. As electrode reactions involve gas, ions and electrons, for an electrode site to be active, access is needed to electronically respectively ioniically conductive phases as well as to open porosity; only at these three phase boundaries reactants can be supplied and products removed. Mogensen (1) described, how fast oxygen transport kinetics improves the oxygen electrode performance, as it increases the active three phase reaction area. The cathode materials used in the solid oxide fuel cell show a high electronical conductivity, however little is known on their ionic conductivity.

The oxygen transport kinetics can be studied by a number of methods including potentiostatic step methods (2) and the isotopic $^{18}\text{O}/^{16}\text{O}$ exchange diffusion profile technique (3).

Thermogravimetrical (TG) methods, too, are well suited for the investigation of oxygen transport kinetics (4-5). Within these methods, information on the diffusion of oxygen is easily available upon varying the oxygen partial pressure of the gas exposing the sample. From TG methods, a separation of bulk diffusion and grain boundary diffusion
may be possible using powdered and compressed samples. Finally, information on the oxygen non-stoichiometry may be obtained from TG experiments.

The main limitation of the TG-methods, however, is their linkage between oxygen diffusion and oxygen stoichiometry variations; the methods are not applicable in the absence of stoichiometry variations.

In the presentation at hand a coulometric titration method will be described, which allows the investigation of transport of oxide ions as the minority charge carriers of mixed conductors, even under small oxygen stoichiometry variation conditions. Following a feasibility test on cerium gadolinium oxide, the method will be used for an investigation of oxide ion conduction in lanthanum strontium manganites.

**Coulometric titration**

For the coulometric titration/transference number method in this work an experimental setup is used, in which current is passed across a ceramic sample, exposed on each side to a small gas volume of fixed oxygen partial pressure. The oxygen partial pressure is controlled potentiostatically, using yttrium stabilised zirconia elements as separators and ambient atmosphere as reference. Upon passage of current across the ceramic sample, oxide ion conduction gives rise to transport of oxygen between the sealed gas volumes. As the oxygen partial pressure in the two volumes are controlled potentiostatically, the oxygen transport is compensated. The oxygen transport number for the ceramic sample is then found as the ratio between the compensating current across the zirconia samples and the overall current across the ceramic sample.

A schematic of the setup used for coulometric titration experiments is shown in figure 1.

**Oxygen transference number and diffusion coefficient**

The variation of the compensating current is related to the passage of current across the ceramic sample. The compensating currents are observed, as oxygen is removed from one gas volume and supplied to the other gas volume. The oxygen ion transference number can be found as the ratio between the compensating current ($I(O^2)$) and the total current ($I_{total}$), as shown in [1] (6):

\[
  t(O^2) = \frac{I(O^2)}{I_{total}}
\]

[1]

As the compensating current, however, is superpositioned onto several additional current phenomena, the transference number is found from the variation of the compensating
current upon reversing the direction of the current across the ceramic sample. The transference number can then be calculated from relation [2]:

$$t(O^{2-}) = \frac{\Delta I(O^{2-})}{\Delta I(tot)}$$  \[2\]

The transference number relates the specific ionic conductivity ($\sigma(O^{2-})$) and the specific overall conductivity ($\sigma(tot)$) as shown in relation [3] (6):

$$t(O^{2-}) = \frac{\sigma(O^{2-})}{\sigma(tot)}$$  \[3\]

From the molar specific ionic conductivity ($\lambda(O^{2-})$) and the Nernst-Einstein equation [4] the oxide ion self diffusion coefficient $D_{self}(O^{2-})$ can be calculated (7):

$$D_{self}(O^{2-}) = \frac{RT}{z^2F^2} \cdot \lambda(O^{2-})$$  \[4\]

The thermodynamic enhancement factor (TEF) relates $D_{self}(O^{2-})$ to the chemical diffusion coefficient $D_{chem}(O^{2-})$ (2):

$$D_{chem}(O^{2-}) = D_{self}(O^{2-}) \cdot TEF$$  \[5\]

The thermodynamic enhancement factor $TEF = \frac{d\ln(a)}{d\ln(c)}$ can be found from the relation between oxygen stoichiometry and oxygen partial pressure for the ceramic material.

**Methodical considerations**

In the coulometric titration method, as for the thermogravimmetrical method, oxide ion transport will only take place in the presence of a concentration gradient. Potentially, however, the demand for oxygen stoichiometry variations is much smaller in this method compared to the TG method.

On the other hand, the coulometric titration method is not free of limitations. Due to local heating during experiments, an equilibration of the oxygen stoichiometry of the
ceramic sample may appear. This process may consume or release oxygen in addition to the effect of passing current across the ceramic sample.

Leak currents may appear. Due to gas leaks, at negative potential vs. air, oxygen may leak into the gas volumes, whereas at positive potentials vs. air, oxygen may leak out. As the oxygen partial pressures are controlled potentiostatically, leak currents across the separators counterbalance these gas flux. Leak currents appear along with the compensating currents.

The conductivity of the alumina construction parts may not be neglected. The ohmic resistance between the zirconia separators is of the order of a few MΩ. Therefore, upon passing current across the ceramic sample, a small current may pass across the alumina components. This current may be measured in addition to the oxide ion current passing the ceramic sample.

Current distribution across the ceramic sample should be as uniform as possible, and the contact resistances of the experimental setup should be minimised. Platinum paint can be used for an optimal current distribution across the ceramic sample, however, may lead to rather high contact resistances. In contrast, direct attachment of platinum wires onto the ceramic sample will give low contact resistance, however, poorer current distribution.

These methodical considerations will be taken into account in the interpretation of the results.

EXPERIMENTAL

Materials

Cerium gadolinium oxide (CGO) with 40% of gadolinium substitution was prepared at Materials Department, Risø National Laboratory. CGO was prepared from cerium nitrate and gadolinium oxide by the glycine/nitrate-method (8).

Lanthanum strontium manganites (LSMs) with 0, 5, 10, 15 and 20% of strontium substitution were prepared from acetates by a solid state reaction route, as described by Krogh Andersen et al. (9). These materials were annealed at 1100°C for 24h in air.

Compressed samples of CGO and LSM (Ø=12mm, h=1.5-7mm) were prepared at a pressure of 5 x 10^6N/cm², using PVA as binder. CGO samples were sintered at 1500°C for 5h, the sample density being >90% of the theoretical density. LSM samples were sintered at 1350°C for 2 hours. The density of sintered samples was >5.7g/cm³, corresponding to >90% of the theoretical density.
Experimental setup

All joints between ceramic components were sealed with gold sealings, heated to 1050°C under a load of 20N.

For the main part of the experiments, platinum paint (Demetron, Einbrennplatin 308A) was used as current distributor on the ceramic sample. Connection to exterior equipment was provided by 0.3mm Pt-wires, attached to platinum paint on the alumina tube. The platinum paints of the alumina tube and the ceramic sample were connected across the gold seal. For this type of experiment, ceramic samples of all heights could be used. In a few experiments, 0.3mm Pt-wires were attached directly to the ceramic sample from the exterior. For this type of experiment, only larger samples could be used. The same type of platinum paint was used as electrodes on the zirconia elements. Electrical connection to the zirconia elements was provided by 0.3 mm Pt-wires. In order to eliminate oxygen flux through the side walls, zirconia elements and LSM samples were sealed from ambient atmosphere by pyrex glass sealings. CGO samples were not sealed by pyrex.

The setup for coulometric titration experiments was placed in a quartz tube in a vertical furnace. An HP75000-VXI system was used for the data acquisition.

Coulometric titration experiments

For current passage experiments, oxygen partial pressures of the two gas volumes corresponding to potentials in the ranges (-800)-0 mV vs. air (for CGO) and (-200)-(+50) mV vs. air (for LSM) were applied. The experimental period was 3600s. For t=0-900s and t=3300-3600s, no current was passed across the ceramic sample. For t=900-3300s, currents of 1mA (for CGO) and 1A (for LSM) were passed, the current direction being reversed at t=1800s, t=2700s and t=3000s.

RESULTS

From experiments done on CGO samples, the feasibility of the coulometric titration method was proven. Upon sample equilibration to the applied oxygen partial pressure, leak currents in the range 2μA-50mA stabilised. The absolute level for the leak current pictured the applied oxygen partial pressure, the quality of the gold sealings and changes of the equilibrium oxygen stoichiometry of the sample. Subsequently, upon passage of 1mA across the CGO sample, a symmetrical pattern of compensating currents of 1±0.1mA was observed in addition to the leak currents. The compensating currents reflected the transport of oxide ions from one sealed volume to the other with an oxide ion transference number close to one.
In figure 2 is shown the current across the two zirconia elements upon passing current of 1A across a compressed sample of La$_{0.85}$Sr$_{0.15}$MnO$_{3+8}$ at 1000°C. In the example displayed, the oxygen partial pressure of the gas volumes corresponded to a potential of 0 mV vs. air. Due to a low oxide ion conductivity of LSM compared to CGO, a number of additional phenomena was observed:

1) In the coulometric experiments with LSM, leak currents in the range (-100)-(+500) μA stabilised. Upon passage of current across the LSM sample (t=900-3300s), a change in the basis level for this leak current was observed together with a sample heating. As the sample is heated during passage of current, the equilibrium oxygen stoichiometry is changed and therefore compensated.

2) The symmetric variations of the compensating current (t=1800s, t=2700s and t=3000) are in the order of a few μA.

3) For LSM samples with 0-20% of strontium substitution level, no significant differences in the compensating current were found. From currents observed, the oxide ion transference number was found as $1.5 \times 10^{-6}$ at 1000°C. From $\sigma_{\text{total}} = 10^2 \text{ S cm}^{-1}$, the corresponding chemical diffusion coefficient $D_{\text{chem}}$ was found as $5 \times 10^{-8} \text{ cm}^2/\text{s}$.

4) The compensating current was found to be independent on the oxygen partial pressure of the gas volumes.

5) Compensating currents as well as leak currents decreased by a factor of 7-8 upon decreasing the temperature from 1000°C to 880°C.

6) The compensating current showed a linear dependency on the current passed across the LSM sample.

7) The main part of the overall sample resistance was made up by contact resistance. Comparing samples with different overall resistances it was found, that the compensating current varied linearly with the overall resistance.

**DISCUSSION**

**Methodical evaluation**

The methodical feasibility was proven from the investigations on CGO. For the investigation of LSM the results are only indicative; for such low ionic conductivity, the method is at its limit. The fact, that the compensating current varied linearly with the overall resistance, indicates, that the ohmic resistance of the alumina construction parts cannot be neglected. Contrary, the resistance of the alumina parts of a few MΩ is lower than the ionic resistance of the LSM sample, and the observed compensating currents are dominated by currents passed across the alumina parts. It is therefore concluded, that
the ionic conductivity of LSM was below the detection limit of the method, and that the transference number and the chemical diffusion coefficient given represent upper limits.

At this point it should be emphasised, that the main potential of the method is its ability to obtain information on transport of oxide ions as the minority charge carriers of mixed conductors. Considering CGO, the oxide ion is the majority charge carrier, whereas electrons are the minority charge carrier. Therefore, although highly suited for the demonstration of oxide ion transport, only little information on the mixed conductivity of CGO can be obtained from the method. In LSM, on the other hand, the oxide ion is the minority charge carrier, and, when within the detection limit, precise information on the mixed conductivity can be obtained.

Comparison to results found from thermogravimetric experiments

In an earlier work by Kjær et al. (5), thermogravimetry was used to study the oxygen diffusion in powdered and compressed samples of LSM. The oxygen diffusion was followed upon changing the oxygen partial pressure exposing the sample. At 1000°C, compressed samples with no open porosity showed faster diffusion compared to powdered samples (10^9 cm^2/s vs. 10^{12} cm^2/s). For powdered samples, the diffusion is believed to be a pure bulk phenomenon, whereas grain boundary diffusion is believed to be predominant in compressed samples.

The information on diffusion coefficients obtained by coulometric titration can be used as a supplement to the results from the thermogravimetical experiments; the oxide ion diffusion coefficient for compressed samples of LSM is no higher than 5 \times 10^8 cm^2/s, a finding supporting the one from thermogravimetry.

CONCLUSION

In the present work the determination of oxide ion transference numbers in compressed ceramic samples by coulometric titration was described. From investigations of cerium gadolinium oxide, the method feasibility was proven. The ionic conductivity of LSM was below the detection limit of the method, and the transference number and the chemical diffusion coefficient reported therefore represent upper limits.

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Figure 1: Schematic of the experimental setup used for the coulometric titration/transference number method.
Figure 2: Current as observed across the two zirconia separators upon passage of a current of 1A across a sample of La$_{0.85}$Sr$_{0.15}$MnO$_{3+δ}$ at 1000°C. Current was passed across the sample at t=900-3300s. The oxide ion transference number is calculated from the symmetrical variations of the compensating current at t=1800s, t=2700s and t=3000s.