**COMPARISON BETWEEN THE THEORETICAL AND PRACTICAL PERFORMANCE OF CERAMIC MEMBRANES IN OXYGEN GENERATION**

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**ABSTRACT**

The separation of oxygen from air can be achieved by incorporating ceramic membranes into high temperature electrochemical devices. Using membrane electrode assemblies consisting of oxygen ion conducting electrolytes \((\text{CeO}_{0.9}\text{GdO}_{0.1}\text{O}_{1.95})\) and perovskite electrodes \((\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3})\), we have been able to produce oxygen within an electrically driven device. In this paper we discuss the performance of these membranes in terms of their electrical characteristics (area specific resistance, current densities) and corresponding oxygen flux outputs. Our initial, performance figures are compared to anticipated theoretical values.

**INTRODUCTION**

At present, there is substantial industrial interest in the use of ceramic membranes to generate oxygen for a variety of applications. NASA, for example, are developing such technology for proposed life support on Mars (1). Oxygen can be used for partial oxidation reactions such as methane to produce synthesis gas (syngas), the ultimate aim being the conversion of natural gas into liquid fuel, a more economically favorable proposition in remote areas (2).

Interest extends into compact electrically driven separators largely for medical and aerospace applications. The elevation of oxygen levels in breathing apparatus, for example, at high altitude is a prerequisite for life support. A small, onboard device that could produce continuous supplies of oxygen is highly desirable, not only reducing the space and weight requirement inherent in the pressure swing equipment currently adopted, but would obviate the need to store gaseous or liquid oxygen on board an aircraft. Performance is also independent of supply air temperature and pressure (altitude). A 100 % oxygen product could be produced in a single operation irrespective of air feed contaminants since the membrane acts as a physical barrier.
The technology for oxygen separation is at a stage where the scientific concepts have been proven, but have not, to date, been exploited to any great extent in the practical sense. In this paper, we present promising initial performance results from a device known as a Ceramic Oxygen Generator (COG). The COG incorporates all solid state components and technology including a gas-tight ceramic membrane sealed within a carbide-strengthened Ni-based superalloy body. The operating temperature can range between 700-1000 °C, however it will be the focus of this paper to discuss the performance of membranes at 800 °C.

**OPERATING PRINCIPLE**

An oxygen separator is based on the concept of an oxygen ion conducting electrolyte through which oxygen ions migrate from one electrode to the other. When an electrical potential is applied across this electrolyte via two porous electrodes, oxygen is dissociated and reduced at the cathode. It then travels through the electrolyte as an oxygen ion, is then oxidised and recombined at the anode to produce oxygen. An external electrical connection allows the transfer of electrons from the anode to the cathode. See Figure 1.

![Figure 1. Schematic diagram of oxygen separator.](image)

A pre-requisite for these electrode-electrolyte-electrode assemblies (membranes or trilayers) is that they are fabricated from oxides in which oxide ion mobility is very high.
MEMBRANE COMPONENTS AND FABRICATION

Our ceramic membranes (trilayers) consist of tape cast electrolytes and screen printed electrodes. The electrolytes are made of 10GCO (Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$) from powder supplied by Rhone Poulenc and are produced by the following fabrication route:

1. Suspension preparation of ceria powder
2. Tape casting the suspension by Doctor Blade method
3. Cutting the appropriate sized foils from the dried tape
4. Sintering of the foil at 1500°C for 1 hour

Ceria electrolytes of 200 μm thickness have been produced of area 5 x 5 cm$^2$. A screenprint paste is then prepared from LSCF powder also supplied by Rhone Poulenc to make the electrodes. The paste is screen printed on both sites of the electrolyte. The electrodes have a composition of La$_{0.6}$Sr$_{0.4}$Fe$_{0.8}$Co$_{0.2}$O$_{3}$, a thickness of 45 μm and a porosity of 55 vol %. Sintering of the electrodes by a co-firing process at 1100 °C for one hour completes the membrane fabrication.

MEMBRANE TESTING APPARATUS

Alumina cell configuration

The I-V characteristics of the membranes, at the membrane manufacture stage, were obtained at an operating temperature between 700-800 °C in air by means of the Solartron electrochemical interface SI 1287. Oxygen flux data was obtained by placing membranes within an alumina cell housing with air on the feed side and helium as carrier gas on the permeate side. Samples could be taken from the permeate site to be analysed by means of gas chromatography using a Perkin Elmer Autoscan XL in combination with a PE Nelson integrator. The membrane was operated using a Delta electronic load that was controlled by a ProDigit potentiostat.

The working device

Bottled air at a fixed flow rate, usually 100 ml/min was introduced into the device using mass flow controlled apparatus. The air supply traverses across the “feed-side” of the membrane and the resulting oxygen-depleted air exits back out the device. The oxygen produced exits a product outlet on the other side of the membrane in the familiar “cross-flow” design (3). At present, we have only looked at single membrane devices. The device (4) has been successfully tested to more than 400 hours of continuous operation.
RESULTS

Membrane performance in terms of oxygen flux, current densities and area specific resistance (A.S.R.) is presented here and is compared to three separate sets of data. Theoretical values based on the known electrical properties of the materials, data acquired at the membrane manufacture stage and those measured from the practical working device. All figures relate to an operating temperature of 800 °C.

Theoretical

The flux of oxygen produced by an electrically driven device is directly proportional to the current passing through the electrolyte membrane (5). The required applied voltage (E) is given by:

\[ E = E_o + IR + \eta_1 + \eta_2 \]

where \( E_o \) is the Nernst Voltage, \( IR \) represents ohmic losses, \( \eta_1 \) is the activation polarisation losses at both electrodes and \( \eta_2 \) represents concentration polarisation losses at both electrodes. Applied voltages of 0.5 V can generate currents around 0.5 A cm\(^2\). This corresponds to

\[ 1 \text{ A.cm}^2 = 3.5 \text{ ml/min.cm}^2 \text{ oxygen} \]

or alternatively,

The quantity of oxygen produced by a current of 1 A is given by

\[ O_2 \text{ (ml/min)} = 60V_{mol}/4F \]

where \( V_{mol} \) is the molar volume of oxygen

\[ F \text{ is Faraday's constant} \]

From alumina cell configuration

Figure 2. represents the relationship between oxygen flux as a function of applied voltage. The results are those collated from the alumina cell configuration at the membrane testing stage after manufacture. The data at 800 °C is depicted by the square markings while the other line represents the values obtained at 700 °C for comparison.
A membrane A.S.R of 0.48 \( \Omega \text{ cm}^2 \) was calculated at 800 °C corresponding to 3.4 ml \( \text{O}_2/\text{cm}^2\text{min} \) at 400 mV.

**From the working device**

The collated data, thus far, from our working devices indicates that the membranes perform satisfactorily both mechanically and electrically over extended periods of time under a variety of operating conditions. Membranes have been driven at 20 A without any obvious deleterious effect on mechanical integrity. Initial demonstrations have shown that performance degradation is observed after approximately 200 hours of operation but is suspected to be the result of alloy oxidation rather than any drop in electrical performance of the membranes themselves. Figures 3. and 4. show the typical voltage-current characteristics and product flow rate vs. current relationship as observed. Flow rates were measured by a bubble flow meter, an input air flow rate of 100 ml/min was used in all cases.
Figure 3. Typical voltage-current characteristics (total across the device) of a single membrane device at 800 °C and an input air flow rate of 100 ml/min.

Figure 4. Typical product flow rates as a function of total current at 800 °C and an input air flow rate of 100 ml/min.

Comparison of results

In the working device, if we assume the minimum active electrode area of the membrane to be 3.6 cm$^2$, presenting the best possible scenario then current densities range from 0.17 to 1.83 A.cm$^{-2}$, from 100mV to 1000 mV total voltages respectively. Figures are calculated from actual voltages across the membrane. This gives A.S.R. values of 0.58 and 0.38 Ω.cm$^2$ respectively. In comparison, area specific resistances associated with the alumina cell configuration are slightly higher than those calculated for the device, for example at 400 mV we have 0.51 Ω.cm$^2$ (alumina cell) compared to 0.48 Ω.cm$^2$ (device).
In terms of oxygen flux, comparison can be made between the manufacture stage and device by perusing Table 1.

| Voltage (mV) | Oxygen Flux* (ml/min.cm²) | Oxygen Flux# (ml/min.cm²) |
|-------------|---------------------------|---------------------------|
| 100         | 0.85                      | 0.61                      |
| 200         | 1.70                      | 1.50                      |
| 300         | 2.55                      | 1.67                      |
| 400         | 3.40                      | 1.86                      |
| 500         | 4.24                      | 2.86                      |
| 600         | 5.09                      | 3.47                      |

Table 1. Oxygen flux as a function of total applied voltage.

where * and # refer to membranes at the manufacturing stage and in the device respectively.

Operating temperature is 800 °C in all cases.

In all cases, the oxygen flux determined from the working device is lower than that calculated from the alumina cell. A plot of the above results would reveal linearity with regards to the alumina cell configuration and not in the actual device. Such irregularity in the latter may be the result of experimental error including possible discrepancies in flow rate measurements. It is true to say however that at lower applied voltages the results between the two configurations are compatible.

The calculated figures measured from the device correspond remarkably closely with those established theoretically, for example a current density of 1.01 A.cm⁻² corresponding to 3.47 ml/min of oxygen from the device. We suggest that the actual figures will be inferior to those accepted theoretically as one would expect. The similarity presented here is a result of figures being based on the lowest possible active electrode area. It is our intention to establish a more accurate figure for the active electrode surface area and hence report flux and current density figures with more confidence. At present we have not been able to ascertain reliably the active contribution from areas of the electrode coated with other materials which are part of the device. These other materials remain commercially sensitive at present.

Given that the maximum active electrode area is 6.3 cm², we suggest that the actual figure will be somewhere between the maximum and minimum. If the mean area is taken (4.95 cm²) then a reduction in the oxygen flux figures in Table 1. for the device of between 20-30 % could be expected.
CONCLUSION

We have shown that the performance figures obtained for ceramic membranes within a practical, electrically drive device are only slightly inferior to theoretically established figures although it is recognized that our figures are based on the optimum current densities that could be achieved.

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