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Structure, properties and performance of functional perovskite membranes

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Acknowledgement/Preface

In this report two abstracts of contributions to the International Conference on Solid State Ionics (SSI-15) held in Baden Baden, July 2005 are presented. They are the result of a collaboration between the University of Twente and the Energy research Centre of the Netherlands, within the project "Bench scale keramische membraan unit voor zuurstofbereiding uit lucht". This work is supported by Dutch Ministry of Economic Affairs through the EDI (Energiebesparing Door Innovatie) program, administered by SENTERNOVEM, under contract no. 02106

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Abstract

The main conclusions from the work presented are:

- Two different membranes with an oxygen flux of ~13 $ml \cdot cm^{-1} \cdot min^{-1}$. were prepared.
- The dilatometric measurements show clearly that the coefficient of thermal expansion is strongly dependent on the atmosphere and temperature.
- The suppression of brownmillerite phase formation in $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ by Ba-doping increases the temperature and pO_2 range for oxygen transport in these materials.

Contents

1. THE PREPARATION OF THIN FUNCTIONAL MEMBRANES FOR THE PRODUCTION OF OXYGEN

Keywords: Perovskite, mixed conductors, oxygen production, functional membranes

Introduction

Dense ceramic materials exhibiting mixed-ionic and electronic conductivity can be used in membranes for the production of oxygen of very high purity. Such a membrane system holds the promise of being energy efficient in comparison with cryogenic distillation and especially pressure swing adsorption techniques. Currently, the most promising membrane material is the perovskite with general formula (Sr/Ba/La)(Co/Fe)$O_{3-\delta}$. The interest in the ionic and electronic conductivity of this family of compounds has grown since 1985 [1], and from that time a large number of papers has been published. Our main aim was to prepare a membrane that could reach a flux of 10 ml·cm^{-1}·min^{-1} and produce about 200 ml·min^{-1} O_2. To this end we have selected the most promising materials, prepared relatively thin (~200 μm) and large (~25 cm^2 surface area) membranes, and performed tests under optimal conditions.

Experiments

The perovskites with composition $Sr_{0.4}La_{0.6}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (SLC2F), $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCF), $Sr_{0.5}Ba_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (SBCF), $Sr_{0.8}La_{0.2}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (SLCF), and $Ba_{0.8}La_{0.2}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BLCF) were purchased from Praxair Speciality Products. Dense membranes were prepared by tape casting, followed by a calcination step at ~1100°C. A mixture of O_2/N_2 was supplied on the membrane feed side. The pO_2 was controlled to be 0.1, 0.2, 0.5, or 1 bar and Helium was used as a sweep gas The application temperature of these membranes requires a sound understanding of the thermal expansion. The coefficient of thermal expansion (CTE) of SCF was measured in He, with a pO_2 of ~10^{-5} bar, and in air, up to 1000°C.

Results and Discussion

In Figure 1, we present the oxygen fluxes measured for the different perovskites. The flux increases in the order: SLC2F < BLCF ~ SLCF < SBCF ~ SCF. The change in the observed oxygen fluxes as a result of the incorporation of La in the perovskites is much larger than that of Ba. The oxygen fluxes increase with increasing pO_2. The highest oxygen flux measured is ~13 ml·cm^{-1}·min^{-1} for SCF and SBCF. This value is much higher than those previously reported, viz. 1 ml·cm^{-1}·min^{-1} [2]. The most important reason for our high fluxes is in the application of thin membranes.

The CTE measured under helium is negative at ~700°C which is not observed in air. In the whole temperature region studied, the CTE is significantly higher in air than in helium. The occurrence of major changes in the CTE of SCF with temperature and pO_2, shows that an average value over a large temperature range has no usability.

Conclusions

We have successfully prepared two different membranes with an oxygen flux of ~13 ml·cm^{-1}·min^{-1}. The dilatometric measurements show clearly that the coefficient of thermal expansion is strongly dependent on the atmosphere and temperature. This implies that the use of an average value over a large temperature region is prone to yield the wrong conclusion in the assessment of technical feasibility

Acknowledgements

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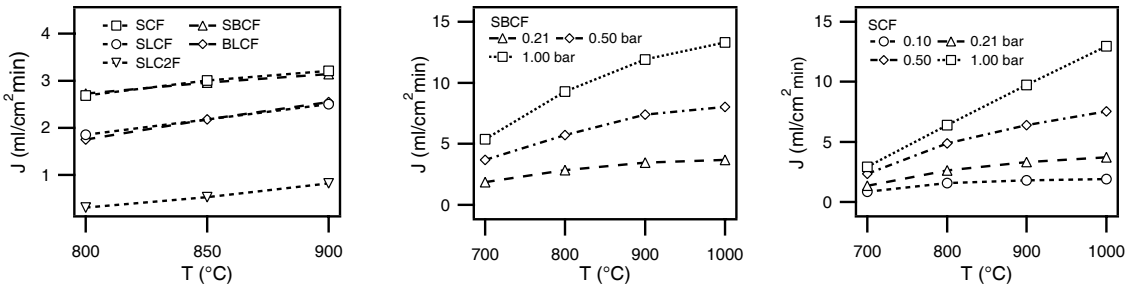

Figure 1: *The oxygen fluxes of SLC2F, SCF, SBCF, SLCF, BLCF as a function of temperature (feed pO_2 = 0.21 bar)(left);and those of SCF (middle) and SBCF (right) for different oxygen partial pressures at the feed side.*

References

[1] Y. Teraoka, et al. Chem. Lett. (1985) 1743-6.
[2] S. Li et al. J. of Membr. Sci. 166 (2000) 51-61.

2. STRUCTURE AND PROPERTY RELATIONS OF $Ba_{1-x}Sr_xCo_{0.8}Fe_{0.2}O_{3-\delta}$

Keywords: Barium-doped, Strontium Cobalt Ferrite, Neutron Diffraction, TPD

Introduction

Barium-doped strontium cobalt ferrite (BSCF) is a mixed oxygen anion/electron conducting material considered as a promising candidate as the cathode of intermediate temperature SOFC [1] and mixed-conducting membrane reactors [2].

Experiments

The XRD diffractograms of commercially available powder samples of $Ba_{1-x}Sr_xCo_{0.8}Fe_{0.2}O_{3-\delta}$ with x=1 and x=0.5 (Praxair) were measured as a function of temperature and oxygen partial pressure. For the O_2 TPD measurements, samples were annealed at 1373K and slowly cooled in air (0.5K/min). 0.5g of these powders was then heated in flowing N_2 (<10ppm O_2) and oxygen desorption measured as a function of temperature via a mass spectrometer.

Results and Discussion

It has been shown [3] that the x=1 member of this series undergoes a phase transition below 1073K from the cubic perovskite to the brownmillerite phase with associated ordering of oxygen vacancies. This ordering leads to a sharp decrease in the oxygen ion mobility and limits the application temperature of the material. Recent high temperature XRD measurements performed in our laboratory between room temperature and 1273K under air and nitrogen atmospheres (pO_2 0.21-10^{-5} atm) have demonstrated that $Ba_{0.5}Sr_{0.5}Co_{0.8}FeO$ does not undergo such a phase transition. It is expected that the suppression of oxygen vacancy ordering will result in technologically significant ion conductivities at lower operating temperatures.

The oxygen TPD results are shown in Figure 1, the mass spectrometer signal intensity is a measure of the rate of oxygen release. Both samples show large desorption peaks at 750K. This peak represents the release of excess oxygen in the crystal structure due to the pre-treatment of the sample. As the samples were slowly cooled in air before rapid heating in nitrogen the oxygen stoichiometry of the material is far from equilibrium with the gas-phase. This excess of oxygen is released only when the oxygen transport and exchange kinetics are activated, in this case around 750K.

After this initial release, the oxygen release from the x=1 member rapidly decreases to zero as the structure transforms to the brownmillerite phase with associated trapping of the oxygen ions. Further oxygen release at higher temperature coincides with the transformation back to the perovskite phase. No such phase transformation occurs for the barium-doped sample, which continues to release oxygen up to 1273K.

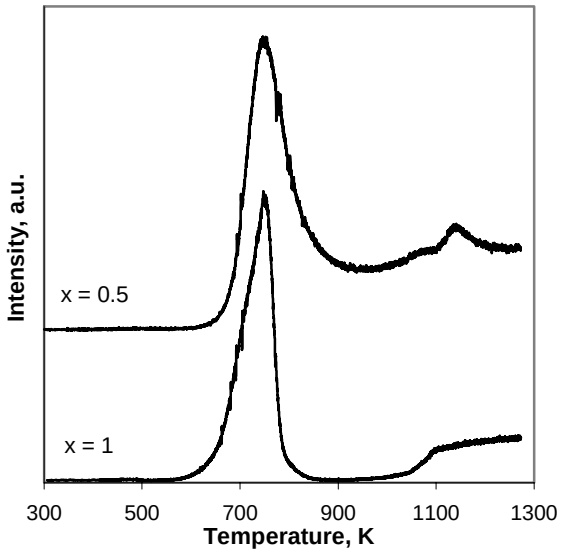

Figure 1: *Oxygen (m/e=32) TPD data for the x=1 and x=0.5 members of the series heated in* N_2

In the coming months the experiments discussed above will be completed for the series to establish where suppression of ordering occurs. This will be complimented by high temperature neutron diffraction measurements to probe the oxygen structure as a function of pO_2 for the x=1 and x=0.5 members of the series. The results of these studies shall be presented at the meeting.

Conclusions

The suppression of brownmillerite phase formation in $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ by Ba-doping increases the temperature and pO_2 range for oxygen transport in these materials.

References

[1] Shao, Z., Haile, S.M., Nature, 431, 170 (2004).
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Appendix A Towards the Application of Functional Perovskite Membranes in the Production of Oxygen

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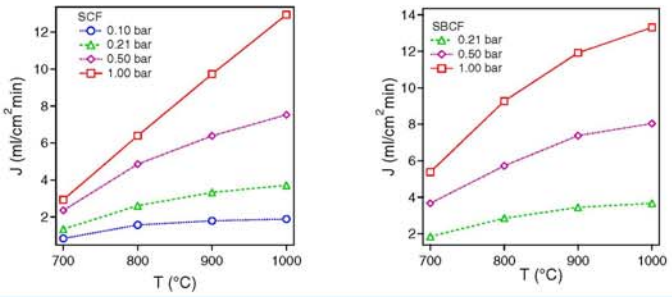
Towards the Application of Functional Perovskite Membranes in the Production of Oxygen

Membrane performance

An economically viable market introduction of perovskite membranes for the on-site stand-alone oxygen production in an energy effective manner requires an oxygen flux of over 10ml·cm^{-2}·min^{-1}. These values have been achieved with 200μm thick functional $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ and $Sr_{0.5}Ba_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membranes with an effective surface area of ~18cm^2.

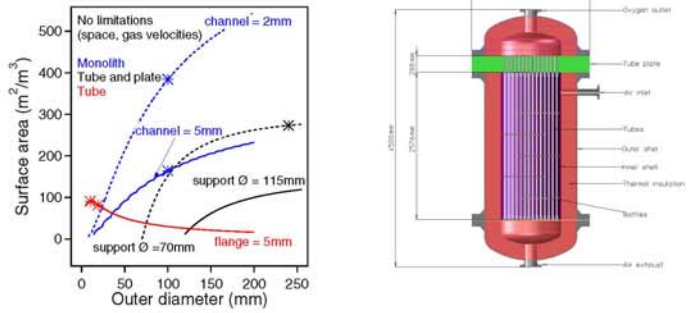


Design of a full-scale module

The economics of this technology is also ruled by the membrane geometry. Factors like surface area per volume, sealing and manifolding are important. The specific surface areas of three concepts were studied:

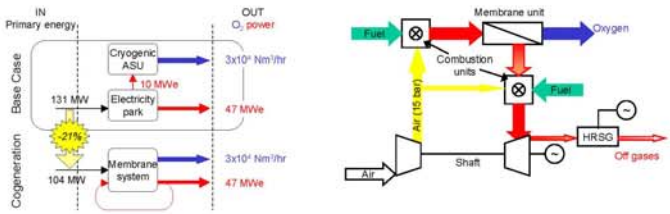
- tubes
- monoliths
- tube-and-plates.

The monolithic system results in the highest specific surface area. With an internal module size of Ø = 1m, L = 2.5m and a maximum gas velocity of 25m/s, the tube concept leads to lowest number of modules (tube: 32; monolith: 39; tube-and-tube: 120).



Process Design: Cogeneration of oxygen and electricity

The optimal operation conditions for a mixed conducting membrane are high temperatures and pressures. It is only a logical step to recuperate the input energy by expanding the hot gasses in a gas turbine, thereby producing electricity.



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