Modeling of High-Temperature Ceramic Membranes for Oxygen Separation

José M. Gozálvez-Zafrilla[1], José M. Serra[2], Asunción Santafé-Moros[1]

Universidad Politécnica de Valencia. 1. Chemical and Nuclear Eng. Depart./ISIRYM

2. Institute of Chemical Technology (ITQ-CSIC)

Introduction

Oxygen separations by ceramic membranes at high temperature will reduce energy requirements and investment cost respect to cryogenic methods and will be thermally integrated in oxyfuel power plants. The process is able to achieve high grade purity.

The high selectivity can be achieved because oxygen separation is based on the transport of oxygen-ion vacancies through the lattice of a crystalline mixed oxide material. The most usual oxygen-ion conducting materials are based on the perovskite structure (ABO3) and comprise Fe/Co/Ni and mixtures of lanthanide and alkali-earth metals in suitable proportions.

The development of these materials requires permeation studies at high temperature, which are usually carried out in lab-scale permeation set-ups (Fig. 1). In these set-ups, an averaged effective coefficient transfer through the membrane is usually obtained by measuring the oxygen transferred to a sweep gas stream. However, the value obtained depends on the geometry of the rig.

Fig. 1. Experimental set-up

Aim

To obtain a model of oxygen transfer in the module useful for estimating parameters from experimental data and for engineering design.

The model is applied to obtain the diffusion coefficient of oxygen vacancies and to study the influence of geometry and experimental conditions in the set-up.

Modelling

Subdomain definition

Three subdomains considered in separated 2D axis-symmetric geometries (Fig. 2):

1. *Permeate*: Sweep gas + small concentration of oxygen (Helium properties)
2. *Membrane:* Oxygen deficient perovskite
3. *Feed:* N_2 (79%)+O_2 (21%)

Constant temperature = 1000 ºC

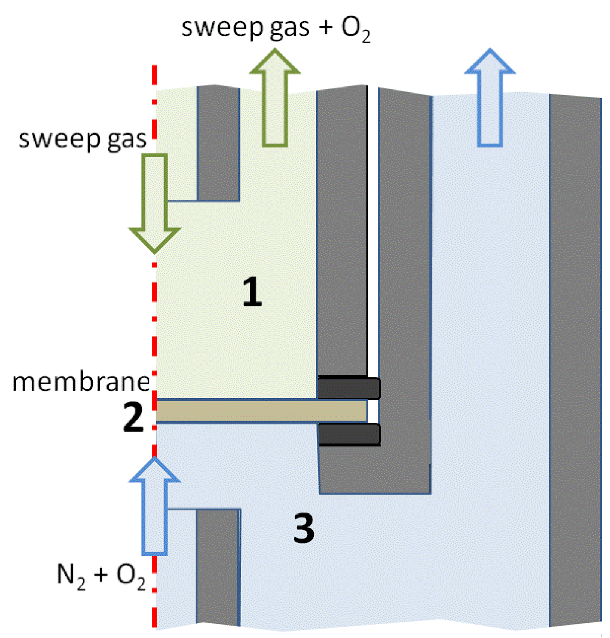


Fig. 2 Subdomains

Governing equations

1. *Permeate*: Incompressible Navier-Stokes and Convection and Diffusion (of O_2)
2. *Membrane*: Diffusion (of O_2 vacancies in the matrix).
3. *Feed:* Incompressible Navier-Stokes and Maxwell-Stefan diffusion (O_2/N_2)

Boundary definition

Incomprensible NS modes:	Diffusion modes:
inlets: laminar	inlets: fixed conc. / mass fraction
walls: non-slip	outlets: convective flow
outlets: 1 atm	walls: insulation
axis: axial symmetry	axis: symmetry
	membrane interfaces: fluxes from couplings

Couplings at membrane interfaces

Identity boundary conditions:

Vacancy concentration at membrane walls are calculated from oxygen pressure using an interpolation function created from pre-calculated equilibrium.

Boundary extrusion variables:

Flux of oxygen and flux of vacancies are interchanged between membrane and the gases.

Meshing and Solver

Meshes: 237/392/2502 elements, locally refined.

Direct solver (UMFPACK), stationary.

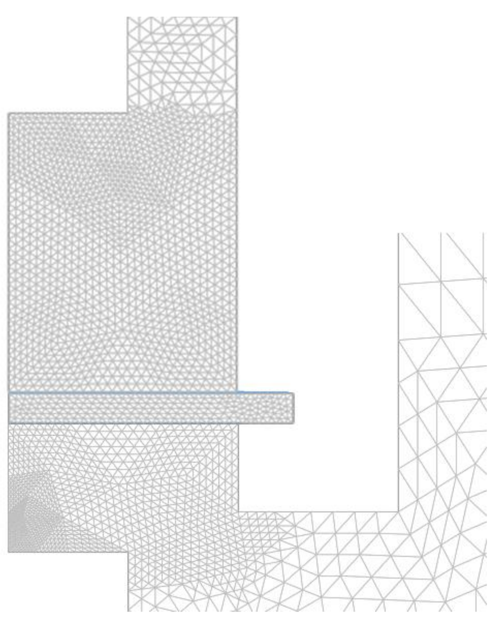


Fig. 3 Meshes

Literature

1. Bart, A. van Hassel et al., *Oxygen permeation modelling of perovskites*, Solid State Ionics, 66, 295-305 (1993)
2. COMSOL AB, *Chemical Engineering Module User's Guide*, 118-256, (electronic document) (2008)
3. J. A. Wesselingh and R. Krishna, *Mass Transfer in Multicomponent Mixtures*, Delft University Press (2000).

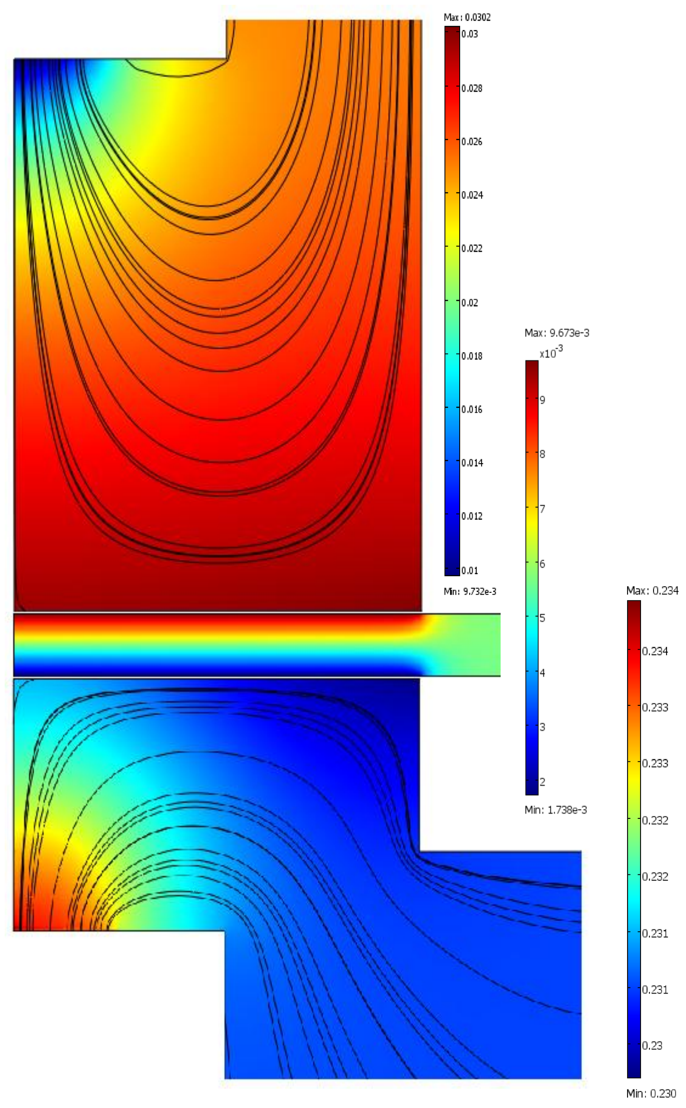
Conclusions

- A model to study the transfer of oxygen in module of ceramic membrane working at high-temperature has been developed.
- The diffusion coefficient of oxygen vacancies in the membrane material could be obtained using the model and experimental results. This value is representative of the performance of the material and can be used to design industrial ceramic modules.
- The effects of experimental conditions and geometry on the performance of the characterization set-up were studied. A significant effect of the membrane seal was found.

Results

The DSPM was successfully implemented either using the "Convection and diffusion" or the "PDE coefficient form" modes.

Fitting of vacancy diffusion and concentration profiles



- The diffusion coefficient of oxygen vacancies D_{vo} could be fitted by matching value of the experimental flux data using quadratic interpolation.
- The diffusion coefficient D_{vo} is an important parameter for design purposes.
- Fig. 4 shows the oxygen concentration and mass fraction for subdomain 1 and 3 and the vacancy concentration for subdomain 2. (Note that the higher vacancy concentration correspond to the lower oxygen concentrations.

Fig. 4 Concentrations and streamlines

Parametric studies

- Lack of homogeneity of the oxygen concentration on the membrane interface and of oxygen flux (important effect of seals) (Fig 5 and 6)
- Approaching the inlet to the membrane causes less homogeneous oxygen distribution on the surface (Fig. 7)

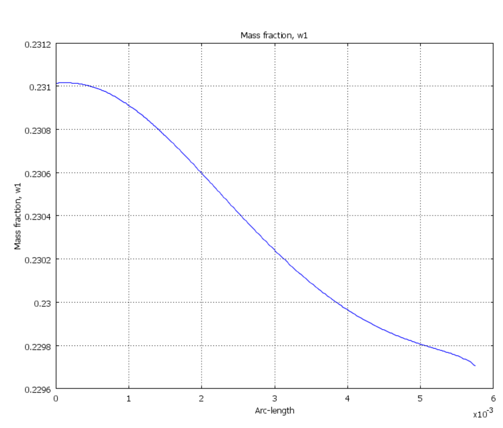


Fig. 5 Mass fraction of O_2 at the membrane interface

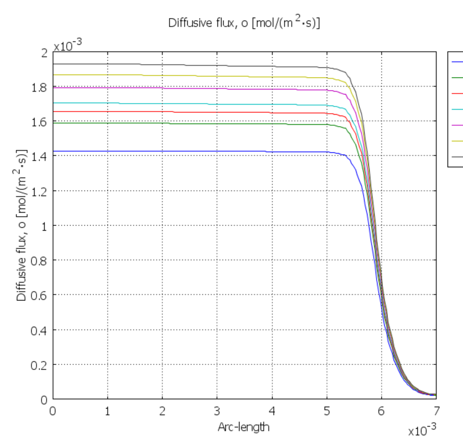


Fig. 6 Flux of O_2 at different gas flows

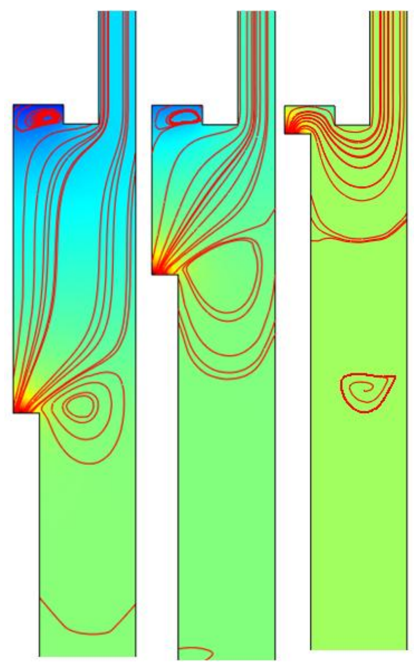


Fig. 7 Effect of inlet position

Acknowledgements

The Spanish Ministry for Science and Innovation (Project ENE2008-06302) and the Conselleria d'Educació de la Generalitat Valenciana (Project GVPRE/ 2008/334) are kindly acknowledged.

For further information

José M. Gozálvez Zafrilla
Universidad Politécnica de Valencia.
Chemical and Nuclear Eng. Depart. (DIQN)
C / Camino de Vera, s/n.
46022. Valencia (Spain)
E-mail: jmgz@iqn.upv.es

COMSOL CONFERENCE 2009
OCTOBER 14-16 2009, MILAN, ITALY