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# Stress analysis and fail-safe design of bilayered tubular supported ceramic membranes

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A B S T R A C T

Supported ceramic membranes based on mixed ionic and electronic conductors are a promising technology for oxygen separation applications. In addition to chemically induced stress under oxygen activity gradients in the materials, strain mismatch between membrane and support gives rise to considerable stress that may compromise mechanical reliability. This paper presents an analysis of stress generated in tubular supported membranes during operation. Closed-form analytical solutions for stresses due to external pressures, strain gradients, and mismatch in materials properties are derived. Stress distributions in two membrane systems have been analyzed and routes to minimize stress are proposed. For a $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membrane supported on a porous substrate of the same material under pressure-vacuum operation, the optimal configuration in terms of minimizing the risk of fracture by ensuring only compressive stresses in the component is achieved by placing the support on the feed side of the membrane. For a $Ce_{0.9}Gd_{0.1}O_{1.95-\delta}$ membrane on a MgO support, stress due to thermal strain mismatch is as large as that due to oxygen activity gradient. Tailoring the thermal expansion coefficient of the support is an effective method to alleviate the total stress. Failure criteria for membrane fracture under compression are thereafter presented. It is found that the tolerable flaw size for fracture in compression is in the millimeter range for both membrane systems at operating conditions in the range of practical interest.



## 1. Introduction

Materials exhibiting mixed ionic and electronic conductivity have potential applications in gas separation technologies. For instance, ceramics that conduct both oxide ions and electrons can be used for selective net transport of oxygen through a membrane. The oxygen can be used in oxy-fuel combustion in power plant processes designed for carbon capture and storage [1,2], or used in catalytic membrane reactors to produce syngas [3,4]. The achievable oxygen flux is limited partly by the loss of driving force over the membrane, and therefore an efficient design in terms of optimizing the flux would require the membrane to be as thin as possible. An obvious design is to support a thin membrane on a substrate that provides the necessary stiffness for handling and for carrying loads in case of an absolute pressure difference exists over the membrane. The substrate needs to be porous to allow gas access to the membrane. Tubular and planar units with a bilayer architecture have been proposed, but the former has a number of advantages including ease of manufacturing using extrusion and dimensional stability under temperature and oxygen activity gradients.

Stresses build up in both the membrane and the support as the device are exposed to different stress generating loadings during manufacturing and subsequent use. In general, these loadings include externally applied pressure differences, nonuniform temperature distributions, and lattice expansion in the materials under oxygen activity gradients. The various stress generating mechanisms pose material strength requirements that can potentially limit the choice of materials and operating conditions, and place stringent quality requirements on the manufacturing process. It is therefore important to have a general method of analysis to quantify the stresses and assess the effects of different loadings and designs.

Stresses due to lattice strains have received particular attention in the literature. It is known that mixed conducting ceramics experience lattice expansion when oxygen is lost at high temperatures. The volume change, referred to as expansion on reduction [5] or chemical expansion [6], can be expressed by a functional dependence on the change in oxygen non-stoichiometry in the material. In all applications, an oxygen activity gradient exists across the thickness of the membrane and chemical stresses are induced.

Chemical stresses induced under oxygen activity gradients were studied analytically for solid oxide fuel cells interconnects [5,7] and electrolytes [8]. Yakabe et al. [9] and Yakabe and Yasuda [10] performed numerical studies on chemical stress distributions in planar

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solid oxide fuel cell interconnects during transient and steady states. Coupling of oxygen transport and stress was considered in the modeling of chemical stress by Krishnamurthy and Sheldon [11] for planar and Swaminathan and Qu [12] for tubular geometry.

For oxygen separation membranes, Atkinson and Ramos [13] applied a simple defect model to calculate the non-stoichiometry profiles through oxides with either predominant ionic or electronic conductivity and plotted the resulting chemical stresses in planar and tubular membranes subjected to different boundary conditions. Blond and Richet [14] studied numerically thermal and chemical stress distributions in a tubular membrane. In their analysis, temperature and oxygen partial pressure fields were first computed by solving the heat transfer and bulk diffusion equations through the membrane. Stresses corresponding to the computed thermal and chemical strain profiles were then determined using finite element analyses. Zolochevsky et al. [15] investigated effects of surface oxygen exchange kinetics and membrane thickness on chemical stresses in tubular membranes by detailed diffusion modeling incorporated in a finite element solver. Zolochevsky et al. [16] analyzed chemical stresses in hollow fiber membranes under sweep gas, vacuum, and pressure operation modes taking into account both bulk transport and surface kinetics.

Prior studies on tubular membranes have been limited to monolithic designs (i.e. components containing one material only) where stresses are primarily due to the presence of chemical strain gradients. In supported membranes, the mismatch in elastic modulus, thermal, and chemical expansion coefficients between the membrane and support materials create additional stresses that are comparable to chemical strain-gradient induced stresses. Depending on the support configuration and operating condition, critical stresses can be located in the weaker porous support even though the chemical strain gradient is most often minimal in the support. To the knowledge of the authors, no investigation of stresses in bilayered tubular supported membranes currently exist. The present work aims to fill this gap.

To this end, the present study is directed towards understanding the effect of material mismatch on total stresses arising during operation. Closed-form analytical solutions for stress distributions in tubular supported membranes are derived, taking into account the mismatch in material properties. Solutions for stresses in bilayers and multilayers are well known for planar geometry [17–20], but only plane-stress solutions under a uniform temperature change have been given for circular geometry [21,22]. These solutions cannot be directly applied to bilayered tubular supported membranes where stresses are also induced by chemical strain gradients. The closed-form solutions obtained in this study are advantageous for quick exploration of the design space without the need for numerical tools which are more time-consuming.

To illustrate the application of the model for fail-safe design variation, stress distributions in two tubular supported membrane systems are analyzed. The first case is a $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) membrane supported on a porous substrate of the same material under pressure-vacuum operation. The second example is a $Ce_{0.9}Gd_{0.1}O_{1.95-\delta}$ (CGO) membrane supported on porous MgO under sweep-gas operation. Practical routes to minimize stress by operating condition variation, and support material and configuration selection are elucidated. Furthermore, failure of the systems under compressive membrane fracture is analyzed and failure criteria are formulated.

In analyzing the two membrane systems, the non-stoichiometry profile is either based on realistic simplifications or adopted from reported modeling studies. The presented model for stresses in bilayered tubular supported membranes can be readily combined with oxygen transport analyses that model bulk diffusion and surface exchange. It is not the aim of the paper to pursue such details, but readers are referred to [23] for oxygen transport modeling of membranes supported by porous substrates.

## 2. Analysis

The cross section of a tubular bilayer is shown in Fig. 1, where 2 concentric annuli are bonded together. The inner and outer radii of the bilayer are designated $r_i$ and $r_o$, and the radius at the interface $r_f$. Linear elasticity theory is employed to determine the stress distributions in the bilayer. Because of axi-symmetry, all shear stresses vanish and only the radial, tangential, and axial stresses need to be determined. Since long tubes are considered in actual applications and the stresses remote from the ends are of primary interest, plane-strain conditions are assumed.

Stress can generally develop due to absolute pressure differences, non-uniform strains resulting from non-stoichiometry and temperature distributions, and mismatch strains between support and membrane. The elastic properties of each layer are characterized by the elastic modulus $E$ and the Poisson's ratio $\nu$. The inner and outer absolute pressures are defined by $P_i$ and $P_o$. In this work, chemical and thermal strains are assumed to vary with radius only and collectively expressed by the internal strain $\varepsilon_i$,

$$\varepsilon_i(r) = \gamma \Delta\delta(r) + \alpha \Delta T(r), \tag{1}$$

where $\gamma$ is the chemical expansion coefficient, $\Delta\delta$ is the change in oxygen non-stoichiometry from the reference state, $\alpha$ is the thermal expansion coefficient, and $\Delta T$ is the temperature change from the reference state.

To determine the stresses, the bilayer can be regarded as two separate monolithic layers interacting only through the interfacial pressure denoted $P_f$ in Fig. 1. The interfacial pressure $P_f$ obviously depends on the material properties, pressure loads and internal strains of the two layers, and needs to be solved for before the stress distributions in the bilayer can be obtained.

In each layer, well-known linear elastic solutions can be directly applied with $P_f$ as the unknown variable. Under a pressure difference, the stresses as given by Lamé [24] are found by satisfying force balance at any $r$. Since the support layer is loaded by the applied inner pressure $P_i$ and the interfacial pressure $P_f$, the stresses are expressed by

$$\sigma^P_{rr,s} = \frac{P_f r_f^2 - P_i r_i^2}{r_f^2 - r_i^2} - \frac{(P_f - P_i) r_f^2 r_i^2}{(r_f^2 - r_i^2) r^2}, \tag{2}$$

$$\sigma^P_{\theta\theta,s} = \frac{P_f r_f^2 - P_i r_i^2}{r_f^2 - r_i^2} + \frac{(P_f - P_i) r_f^2 r_i^2}{(r_f^2 - r_i^2) r^2}, \tag{3}$$

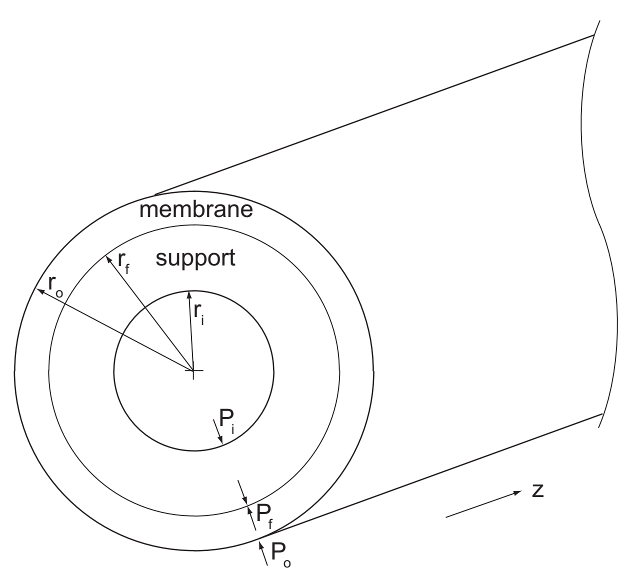


**Fig. 1.** Cross section of a tubular bilayer.