

Chemical Expansivity in Ceramic Oxygen Transport Materials

Mark R. De Guire, Case Western Reserve University, Department of Materials Science & Engineering

Abstract

Modular, portable, reliable methane reformers would enable natural gas to be converted to syngas at wellheads, with the potential for subsequent conversion to (for example) higher-value hydrocarbons or hydrogen for carbon-free electricity. Oxygen transport membranes (OTMs) based on mixed electronic–ionic conducting (MEIC) ceramics constitute a critical enabling technology for such systems. These membranes act as electrochemical closed circuits to separate pure oxygen from air to partially oxidize methane (with steam) to CO and H₂. To realize the potential of these devices, the stresses in the ceramics under the oxygen gradients present across the membranes must be mitigated, while still enabling practical levels of oxygen flux.

Chemical expansivity¹ — volume change resulting from a change in oxygen vacancy concentration — is the fundamental cause of stresses in ceramic OTMs. Gradients in oxygen potential (p_{O_2}) from 0.2 on the air side to 10⁻¹⁶ and lower on the fuel side can lead to differential strains of 0.2% or more, sufficient to crack the membrane. If the membrane is made as a porous/dense/porous layered structure,² the porous layers bear some of the volume change, reducing the stress on the dense inner layer without impeding oxygen transport. The objective of the proposed research is to subject candidate ceramic OTM materials to step changes in p_{O_2} and simultaneously measure their oxygen diffusivity and chemical expansivity. Repeating the experiment on porous/dense/porous specimens will serve as proofs of concept and provide insight into the common characteristics of the most promising MEIC materials.

Background

The use of mixed electronic–ionic conducting ceramics (MEICs) as oxygen separation media for advanced reforming of natural gas has been under study since the first patent was issued to Standard Oil / British Petroleum in the late 1980s.³ Since then, the U.S. Department of Energy has funded major efforts to develop reformers (see for example reference 4) based on ceramic oxygen transport membranes (OTMs) and test them at pilot scale. Groups in the U.S., Europe, and Asia have studied these materials for use in various chemical processes in addition to methane reforming. (For a recent review, see reference 5.)

The hurdle that remains to be overcome before this technology can be widely implemented is improving mechanical reliability of the ceramic OTMs, over operating lifetimes of 40,000 h.⁶ The gradient in oxygen potential between the air side (0.2 atm) and the methane side (10⁻¹⁷) creates a gradient in oxygen vacancy concentration, and therefore differential strains, across the membrane thickness,⁷ a phenomenon Adler¹ called *chemical expansivity*. For a uniformly dense membrane, if the oxygen gradient Δp_{O_2} exceeds a critical value, then the resulting stress can exceed the fracture strength of the OTM, leading to mechanical failure. Simply making the ceramic membrane thicker may reduce the stress, but it will reduce the oxygen flux.

These conflicting requirements can be addressed with porous layers of the MEIC material on both sides of a dense layer (Fig. 1b). The engineered porosity gives the porous layers lower effective Young's modulus, so they experience lower stress. They also reduce the Δp_{O_2} across the dense layer so its stress is reduced below the fracture strength, yet keep Δp_{O_2} high enough for practical oxygen flux (typically ≥ 10 sccm cm⁻²).^{17,24} This design strategy lies at the core of a recent patent,² and will be experimentally tested in the proposed research. One of the co-inventors (Dr. Ajit Sane) serves as an advisor on this project.

In addition to mixed conductivity, the requirement for phase stability at high operating temperatures (700–1,000 °C) and wide ranges of oxygen potential places significant constraints on which materials are suitable for OTMs.^{5,6} Currently the most promising candidates fall into two categories of crystal structure: substituted perovskites, e.g. La_{1-x}(M1)_x(M2)O_{3-δ} (M1 = Ca, Sr, and/or Ba; M2 = one or more 3d transition metals, e.g. Ti, Cr, Mn, Fe, Co) and substituted fluorites, e.g. Ce_{1-x}Gd_xO_{2-δ} (CGO). The most widely used perovskites (LSCF, (La,Sr)(Co,Fe)O_{3-δ}; BSCF, (Ba,Sr)(Co,Fe)O_{3-δ}) typically have high oxygen flux, but also high chemical expansivity, whereas the opposite applies to the fluorites. Neither category has proven satisfactory for long-term mechanical reliability. Thus the potential to reduce stresses in the dense layer becomes even more crucial for wider-scale implementation of ceramic OTMs and better utilization of natural gas resources.

Research Progress to Date

At the end of the first year of the project, the researchers (the PI, one M.S. student, and two undergraduate researchers) have established essential experimental capabilities:

- Utilizing aqueous synthesis techniques to synthesize multicomponent (La,Sr)(Co,Fe,Cr)O_{3-δ}

- perovskites (via the amorphous malic acid precursor routes) and substituted ceria (fluorite) powders (via sol-gel coprecipitation). A high level of phase purity in these powders has been confirmed using x-ray diffraction.
- Pressing and sintering of thin, dense ceramic disks of the perovskite powders.
 - Retrofitting an existing Orton 1600D dilatometer with an atmosphere control system (mass-flow controllers, CO detector, valves, and piping) capable of subjecting the ceramic OTM specimens to sequential step changes in p_{O_2} from 0.21 to 10^{-16} .
 - Completing calibration runs on the dilatometer.
 - Acquiring pre-synthesized powders of selected reference perovskite $(La,Sr)(Co,Fe,Cr)O_{3-\delta}$ compositions.

Remaining Work

The project is set to begin the key experiments that will enable simultaneous measurements of the chemical expansivity and the diffusion coefficient of oxygen in these ceramic materials, when they are subjected to step changes in p_{O_2} under isothermal conditions. The dilatometer will measure dimensional change ΔL_t in the long dimensions of the specimen, which will depend on the average oxygen vacancy concentration in the specimen $\langle C \rangle(t)$,

$$\langle C \rangle(t) = \frac{1}{\Delta z} \int_0^{\Delta z} C(z, t) dz \quad (1)$$

The explicit relation for the average concentration $\langle C \rangle(t)$ in terms of time t , half thickness Δz , and diffusivity D_0 is:

$$\frac{\langle C \rangle(t) - C_S}{C_t - C_S} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[\frac{-(2n+1)^2 \pi^2 D_0 t}{4 (\Delta z)^2} \right] \quad (2)$$

Since the relative expansion $(L_t - L_0)/L_0$ is directly proportional to $[\langle C \rangle(t) - C_i] / C_i$ in analogy to thermal stress,¹⁰ measurement of transient relative expansion with time can be used to calculate the diffusivity D_0 for a given thickness.

The chemical expansivity β (assumed constant during the test) is defined as the dimensional change per unit compositional change:

$$\beta \equiv \frac{1}{L_0} \frac{\Delta L}{\Delta \langle C \rangle} = \frac{1}{L_0} \frac{L_t [\langle C \rangle(t)] - L_0 [C_i]}{\langle C \rangle(t) - C_i} \quad (3)$$

Once the diffusivity is calculated from the transient expansion measurements, the concentration profile within the sample and hence the stress profile can be calculated in the same way as for thermal stresses.

Impact of project on professional development

For the PI, this project represents a valuable new research direction within the general field of high-temperature solid-state electrochemistry, as applied to ceramics in critical areas of energy and sustainability. The author is preparing a new NSF grant proposal to continue this work after the conclusion of the PRF funding. For the graduate student, this first year of research has convinced him to pursue a doctoral degree in this field. The undergraduate students, now both sophomores, have contributed significantly to the project (for course credit, unpaid) while gaining hands-on experience in chemical synthesis and applied ceramics research.

1. S. B. Adler, *J. Am. Ceram. Soc.* **84** [9] pp. 2117–19 (2001).
2. A. Y. Sane and T. L. Cable, U. S. Patent No. US 8,834,604 B2, Sep. 16, 2014.
3. T. J. Mazanec, T. L. Cable, and J. G. Frye, Jr., U. S. Patent No. 4,793,904, Dec. 27, 1988.
4. L. L. Anderson, P. A. Armstrong, R. R. Broekhuis, M. F. Carolan, J. Chen, M. D. H. C. A. Lewinsohn, C. F. Miller, J. M. Repasky, D. M. Taylor, and C. M. Woods, *Solid State Ionics* **288** pp. 331–337 (2016). <http://dx.doi.org/10.1016/j.ssi.2015.11.010>
5. A. A. Plazaola, A. C. Labella, Y. Liu, N. B. Porras, D. A. P. Tanaka, M. V. S. Annaland, and F. Gallucci, *Processes* **7** [128] (2019).
6. S. Gupta, M. K. Mahapatra, and P. Singh, *Materials Science and Engineering R* **90** pp. 1–36 (2015). <http://dx.doi.org/10.1016/j.mser.2015.01.001>
7. C. Salles, J. Fouletier, D. Marinha, and M.-C. Steil, *Journal of Membrane Science* **527** pp. 191–197 (2017). <http://dx.doi.org/10.1016/j.memsci.2016.11.083>
8. K. Watanabe, S. Ninomiya, M. Yuasa, T. Kida, N. Yamazoe, H. Haneda, and K. Shimano, *J. Am. Ceram. Soc.* **93** [7] pp. 2012–2017 (2010). DOI: 10.1111/j.1551-2916.2010.03700.x
9. G. H. Geiger and D. R. Poirier, *Transport Phenomena in Metallurgy*, eq. 14.41, p. 487. Addison-Wesley, Reading, Massachusetts, 1973.
10. A. R. Cooper, D. A. Krohn, *J. Am. Ceram. Soc.* **52** [12] pp. 661–664 (1969).