



# SOLID STATE IONICS

by Eric D. Wachsman

**S**olid state ionics (the transport of ions in solids) is not only a major focus of the High Temperature

Materials (HTM) Division but also plays a role in most other ECS Divisions. For instance, the flux of oxygen ions through ceramic Ion Transport Membranes (ITMs) and Solid Oxide Fuel Cells (SOFCs) under open circuit conditions is governed by the Wagner equation:

$$J_{O_2} = -\frac{RT}{16 F^2 L} \int_{\ln(p_{O_2})}^{\ln(p_{O_2}')} \frac{\sigma_e \sigma_v}{\sigma_e + \sigma_v} d \ln(P_{O_2}) \quad (1)$$

where  $J_{O_2}$  is the  $O_2$  flux,  $P_{O_2}$  is the  $O_2$  partial pressure,  $R$  and  $F$  are the gas and Faraday's constants,  $T$  is temperature,  $L$  the thickness of the membrane or film, and  $\sigma_e$  and  $\sigma_v$  are the conductivities of electrons and oxygen vacancies, respectively.

But the growth of oxide films during corrosion (Corrosion Division), involves the same basic mechanism of ionic transport and is governed by the same basic equation. Similarly, the same mechanisms and governing equation describe the growth of oxides for semiconductor device fabrication (Electronics & Photonics Division). However, the corrosion and semiconductor device community typically refers to an integrated empirical form of this equation, the "Parabolic Rate Law."

In addition, the same ion conducting electrolyte used in SOFCs is used in the most prevalent of solid state sensors, the automotive oxygen sensor (Sensor Division). Moreover, batteries (Battery Division) and Proton Exchange Membrane Fuel Cells (Energy Technology Division) also rely on ion transporting materials for their construction and operation. Finally, electrocatalytic phenomena (Physical and Analytical Electrochemistry Division) at the ion-conductor interface are critical to the performance of these devices.

Numerous solid state materials conduct cations (e.g.,  $Li^+$  and  $Na^+$ ) and anions (e.g.,  $F^-$  and  $O^{2-}$ ), among these, activities in the Society's HTM Division tend to focus on oxide ion conducting as well as proton conducting ceramics. These materials are used in, and being investigated for, a wide variety of technological applications (see the other articles in this issue of *Interface*). Their required functionality goes far beyond mechanical strength and toughness, to include such properties as ionic and electronic conductivity, thermochemical stability, and catalytic activity. These latter properties arise out of their defect chemistry and resultant wide range in oxygen stoichiometry. Depending on their defect chemistry and environment, these materials can exhibit exclusively ionic (electrolyte) or electronic conduction, or mixed (both ionic and electronic) conduction. For more information see Refs. 1 and 2.

Ionic conduction involves hopping from an occupied to a vacant lattice (or interstitial) site. Figure 1 shows this process for anion conduction in a fluorite structured oxide and the path taken from one tetrahedrally coordinated site to another.<sup>3</sup> At high temperatures, the ionic conductivity of these solid state materials is comparable to that of aqueous solutions at ambient conditions. For example, at 1000°C the ionic conductivity of yttria-stabilized zirconia (YSZ) is  $0.1 S \cdot cm^{-1}$ , and in fact, there are numerous oxides that have significantly higher conductivity at lower temperatures (albeit with a stability trade-off).

The high conductivity of these materials is attributable to the high concentration of mobile defects: oxygen vacancies ( $V_O^{\bullet\bullet}$ ), oxygen interstitials ( $O_i''$ ), electrons ( $e'$ ), and electron-holes ( $h^\bullet$ ). Each of these defects can be treated as a

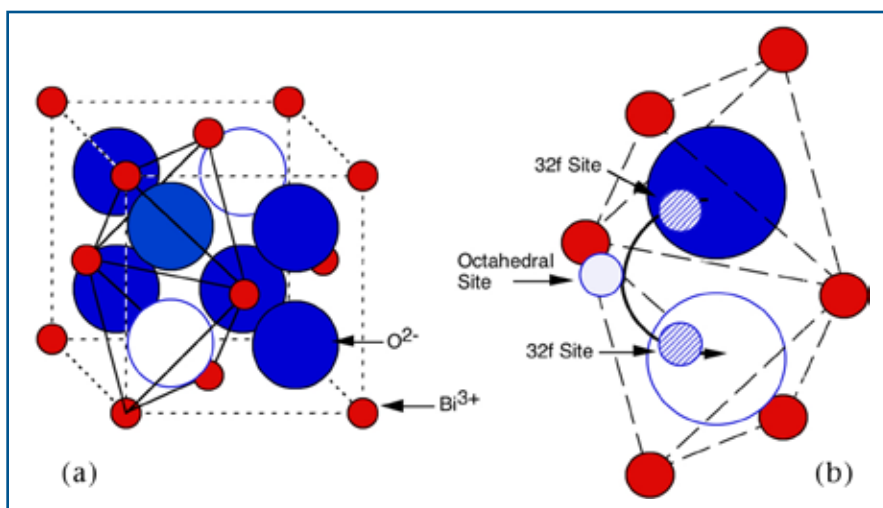


Fig. 1. Anion transport in a fluorite oxide (a) lattice and (b) path (from Ref. 3).

chemical species and their concentration determined from thermodynamics. The result of this is that by evaluating the heterogeneous equilibria between gaseous oxygen and the solid state,

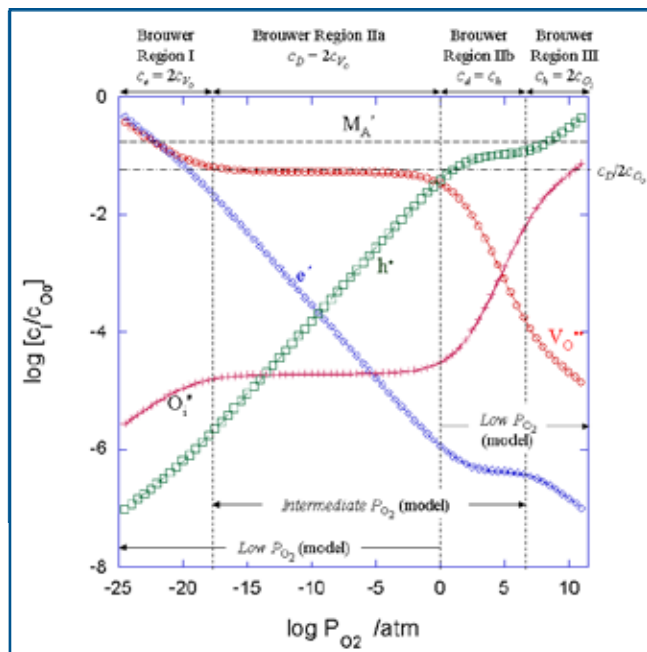
$$O_2^X = 1/2O_2 + V_O^{\bullet\bullet} + 2e' \quad (2)$$

combined with the internal chemical equilibria for ionic defect and electron-hole pair formation and the concentration of aliovalent dopants (such as  $Y^{3+}$  on a  $Zr^{4+}$  site -  $YZr'$ ), one can calculate the concentration of all species as a function of external oxygen partial pressure,  $P_{O_2}$ . This solution for the defect concentrations is shown graphically in a typical electrolyte defect equilibrium diagram, Fig. 2. This diagram shows four "Brouwer regions,"  $P_{O_2}$  ranges over which a pair of defects dominate the neutrality relationship due to their relative high concentration. Thus the same material can exhibit n-type, ionic, and p-type conductivity depending on  $P_{O_2}$ . Each of the mobile species is then transported through the material in response to an applied chemical (due to a  $\Delta P_{O_2}$ ) or electrical potential.

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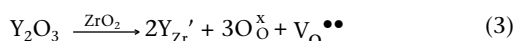
## About the Author

**ERIC D. WACHSMAN** is the Past Chair of the ECS High Temperature Materials Division, Director of the Florida Institute for Sustainable Energy, Director of the UF-DOE High Temperature Electrochemistry Center, and an UF-Research Foundation Professor of Materials Science and Engineering at the University of Florida. Dr. Wachsman's research interests are in ionic and electronic conducting ceramics, from fundamental investigations of their transport properties and heterogeneous electrocatalytic activity, to the development of moderate temperature solid oxide fuel cells (SOFC), gas separation membranes and solid state sensors. He is an ECS Fellow and an Editor of *Ionic*.



**Fig. 2.** Defect concentration dependence on  $P_{O_2}$  for a typical fluorite oxide (from Ref. 4).

Oxide materials such as YSZ, rare earth doped ceria, rare earth doped bismuth oxide, and doped lanthanum gallates have been widely investigated as oxygen ion conductors. Of these materials, YSZ has been most successfully employed. The yttrium oxide dopant serves dual roles: it stabilizes the high temperature cubic phase in zirconia and also generates oxygen vacancies through the following defect reaction:



thus creating more of the conducting species ( $V_O^{\bullet\bullet}$ ).

The high oxide ion conductivity over wide ranges of temperature and oxygen pressure in these materials has led to their use as electrolytes in a variety of electrochemical applications. High temperature solid oxide fuel cells (SOFCs) for electric power generation are now nearing commercialization. Oxygen sensors are widely used in combustion control, especially in automobiles, atmosphere control in furnaces, and as monitors of oxygen concentration in molten metals. Other applications include electrochemical pumps for control of oxygen potential, steam and  $CO_2$  electrolyzers, and high temperature reactors for chemicals production from hydrocarbons. Some of these applications are discussed in the ensuing articles, and as with most recent technological advances, the greatest challenges lie at the ion conducting materials interface and requires the interface between different scientific disciplines. ■

## References

1. *The Defect Chemistry of Metal Oxides*, D. M. Smyth, Oxford University Press, 2000.
2. *The CRC Handbook of Solid State Electrochemistry*, P. J. Gellings and H. J. M. Bouwmeester, Eds., CRC Press, 1997.
3. S. Boyapati, E. D. Wachsman, and N. Jiang, *Solid State Ionics*, **140**, 149 (2001).
4. K. L. Duncan and E. D. Wachsman, *Ionic*, **13**, 127 (2007).

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