EVALUATION OF SOLID OXIDE ELECTROLYTES WITH THE PYROCHLORE STRUCTURE FOR USE IN FUEL CELLS

P.K. Moon* and H.L. Tuller
Crystal Physics & Optical Electronics Laboratory
Department of Materials Science & Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139

ABSTRACT

Compositions in the pyrochlore system Gd$_2$(ZrxTi$_{1-x}$)$_2$O$_7$ (GZT) are examined as possible alternatives to stabilized zirconia as solid oxide electrolytes in fuel cells. The GZT system is shown in general to be a mixed ionic/electronic conductor with the titanate end member being predominantly semiconducting and the zirconate end member achieving intrinsic fast oxygen ion conductivity. A defect model is utilized to assist in the deconvolution of ionic and electronic contributions to the total conductivity. This data is then used to construct electrolytic domain boundaries which are shown to broaden rapidly with increasing x. The key features which make the GZT system attractive as a fuel cell element are discussed.

1. INTRODUCTION

Due to an increased concern with atmospheric pollution and repeated volatility in the supply of fossil fuels, there is a renewed incentive to examine alternative energy conversion approaches which are inherently more efficient and non-polluting. High temperature fuel cells utilizing solid electrolytes are receiving increased attention due to (a) their ability to utilize hydrocarbon fuels resulting from rapid electrode kinetics at elevated temperatures, (b) potential for higher current densities and thereby higher power densities, and (c) the absence of liquids and the attendant problems with electrode wetting, corrosion, and sealing.

High temperature fuel cells utilizing stabilized zirconia as the oxygen-ion solid electrolyte were first seriously considered nearly 25 years ago. In the present address: Intel Corp., Hillsboro, OR 97124-6497

*Present Address: Intel Corp., Hillsboro, OR 97124-6497

Downloaded on 2019-04-29 to 207.241.231.83 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).
interim, most of the attention has been directed towards cell engineering and development and testing of electrodes rather than on alternative electrolytes. Stabilized zirconia still remains the electrolyte of choice although several others including δ-Bi2O3, CeO2, and α-Ta2O5 have been examined from time to time. In this paper, we discuss our findings regarding the transport properties of the pyrochlore solid solution Gd2(Zr1-xTix)2O7 (GZT) in relation to its potential as a solid electrolyte in fuel cells.

Acceptable solid electrolytes must satisfy a number of criteria including high oxygen ion conductivity, low electronic conductivity, chemical compatibility with electrodes and/or substrates, good mechanical strength, thermal shock resistance and imperviousness to gases. Stabilized zirconia has remained the material of choice primarily because of the first two criteria. Its relatively high oxygen ion conductivity (e.g. ~10⁻¹ S/cm at 1000°C) is coupled to an excellent stability with respect to reduction or oxidation, which limits its electronic conductivity to below 1% of the total between 10⁴ < P0₂ < 10⁻² atm. Other materials, such as δ-Bi2O3 and doped CeO2, although they have higher ionic conductivities, reduce much more readily, thereby reducing the size of their electrolytic domains with resultant decreases in output voltage and energy conversion efficiency. Although the GZT system is not generally as conductive as stabilized zirconia at elevated temperatures, it does, as we illustrate below, exhibit a number of attractive features which make it interesting as a solid oxide electrolyte candidate.

The pyrochlore structure has a cubic unit cell with a lattice constant of roughly 10Å and a general molecular formula of A₂B₂O₅X, where A and B are cations and O and X are anions. A diagram of a portion of the pyrochlore structure projected onto the (100) plane is shown in Fig. 1. Detailed descriptions of the pyrochlore structure can be found elsewhere.

The pyrochlore structure is a superstructure of the defect fluorite structure with exactly twice the lattice parameter. Pyrochlore and ideal defect fluorite differ in that pyrochlore has additional ordering on both the cation and the anion sublattices and some of the oxygen ion positions are slightly distorted from their fluorite position. Oxygen vacancies occur at random throughout the anion sublattice in fluorite but are ordered onto particular sites (8b) in the pyrochlore structure.
Structural disorder occurs in pyrochlore compounds when the superstructure ordering, which distinguishes pyrochlore from fluorite, is partially lost. Two types of disorder are prevalent: antisite disorder on the cation sublattice where the A and B cations switch positions and quasi-Frenkel disorder on the anion sublattice where oxygen ions leave their normal sites (8a and 48f) and enter interstitial sites (8b). It is the latter feature which we believe results in intrinsic fast oxygen ion conductivity in a number of pyrochlores including Gd$_2$Zr$_2$O$_7$ and Y$_2$Zr$_2$O$_7$\textsuperscript{12}. Both types of disorder can be expected to occur to a substantial degree for certain compositions owing to the similarity of the fluorite and pyrochlore structures.

Detailed studies of the electrical properties of Gd$_2$Zr$_2$O$_7$ and Nd$_2$Zr$_2$O$_7$, were initiated by Van Dijk et al\textsuperscript{13} who found a local maximum in ionic conductivity (e.g. 5x10^{-3} S/cm at 720°C) and minimum in activation energy (~0.87eV) for the GdO$_{1.5}$-ZrO$_2$ system for 50 mol\% GdO$_{1.5}$, i.e. Gd$_2$Zr$_2$O$_7$. At least for high Gd$_2$O$_3$ levels, the pyrochlore structure gave higher ionic conductivities than neighboring fluorite phases. Comparing conductivities more globally, fluorite compositions can be found which exhibit higher conductivities than the pyrochlore phase, e.g. Gd$_{0.19}$Zr$_{0.81}$O$_{1.905}$ (fluorite) and Gd$_{0.5}$Zr$_{0.5}$O$_{1.675}$ (pyrochlore) exhibit ionic conductivities of 9.3x10^{-5} S/cm and 4.8x10^{-3} S/cm at 723°C respectively.\textsuperscript{14} Attempts to increase the ionic conductivity of Gd$_2$Zr$_2$O$_7$ by acceptor doping have resulted in either no change\textsuperscript{15} or a decrease in conductivity\textsuperscript{16} pointing to the intrinsic nature of the ionic disorder.

Studies of Y$_2$Ti$_2$O$_7$ by Uematsu et al\textsuperscript{17} show it to be a mixed ionic-electronic conductor. In a more complete study, recently completed by the authors on GZT and YZT systems,\textsuperscript{15} the ionic conductivity of the undoped titanate end members was shown to be many orders of magnitude lower than the zirconate end members and strongly impurity dependent. Conversely, the electronic conductivities of the titanates were substantial at elevated temperatures, in contrast to the zirconates. Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$ was found\textsuperscript{12} to exhibit a very large increase in ionic conductivity (~3 orders of magnitude) between x=0.15 and x=0.4 with further substantial increases thereafter. This is illustrated in Fig. 2. At the same time, the electronic conductivity decreases markedly with x > 0.2.\textsuperscript{18} This provides an opportunity to control the mix of ionic and electronic conductivity - a feature of interest in developing electrodes with high oxygen-exchange kinetics.
2. THEORY

Ionic Conductivity. We have previously demonstrated that compositions in the GZT system with \( x > 0.4 \) are intrinsically highly disordered on the oxygen sublattice leading to high concentrations of both oxygen vacancies and interstitials. We have also shown, explicitly for GZT with \( x=0.3, \)\(^{(19)} \) that oxygen vacancies are far more mobile than oxygen interstitials and expect the same to be true for other values of \( x \).

The ionic disorder can be viewed as Frenkel-type in nature which is given by

\[
\text{nil} \Rightarrow V_{o}^{-} + O_{\frac{1}{2}}^{-} \tag{1}
\]

or

\[
[V_{o}^{-}][O_{\frac{1}{2}}^{-}] = K_F(T) = K_F^{\circ}\exp(- \Delta H_F/kT) \tag{2}
\]

where \( K_F(T) \) is the Frenkel equilibrium constant. The oxygen ion conductivity can therefore be written as

\[
\sigma_{i} = 2qK_F^{1/2}(T) \left( \mu_V + \mu_{\text{int}} \right) \tag{3a}
\]

\[
\equiv 2qK_F^{1/2}(T) \mu_V \tag{3b}
\]

where \( \mu_V \) and \( \mu_{\text{int}} \) represent oxygen vacancy and interstitial mobilities, respectively.

Nonstoichiometry and Electronic Conductivity. The reduction reaction which leads to nonstoichiometry and thereby the generation of excess electrons is

\[
O_{o} = V_{o}^{-} + 2e' + \frac{1}{2}O_2(g) \tag{4}
\]

which leads to the mass action relation

\[
[V_{o}^{-}] n^2 P_{O_2}^{1/2} = K_R(T) = K_R^{\circ}\exp(- \Delta H_R/kT) \tag{5}
\]

where \( K_R(T) \) is the equilibrium constant for the reduction reaction and \( P_{O_2} \) the oxygen partial pressure. Combining Eq. 2 with 5, we find the electron density to be

\[
n = (K_R/K_F^{1/2})^{1/2} P_{O_2}^{-1/4} \tag{6}
\]

Since the electron-hole product given by

\[
np = K_e(T) = N_eN_v \exp(-E_g/kT) \tag{7}
\]

is a constant, one readily finds the hole density to be
\[ p = K_e \left( K_F^{1/2}/K_R \right)^{1/2} P_{O_2}^{1/4} \] (8)

The total conductivity can therefore be written as

\[ = A + B P_{O_2}^{-1/4} + C P_{O_2}^{+1/4} \] (9)

where the first term is the \( P_{O_2} \)-independent ionic conductivity given by Eq. 3b, the second term is the electron contribution, \( nq \mu_e \), with \( n \) given by Eq. 6, and the third term is the hole contribution, \( pq \mu_h \), with \( p \) given by Eq. 8. Note, that the three partial conductivities can readily be distinguished by their \( P_{O_2} \) dependencies.

Although ionic defects substantially outnumber electronic defects under all experimental conditions of interest, the electronic conductivity can become appreciable (i.e. \( \sigma_{\text{electronic}} = \sigma_{\text{ionic}} \) at sufficiently oxidizing \( (P_{O_2}=P_p) \) or reducing conditions \( (P_{O_2}=P_n) \) given the much higher electronic mobilities (see Eq's 8 and 6, respectively). \( P_n \) and \( P_p \) are readily established at each temperature by setting

\[ A = B P_{O_2}^{-1/4} \] (10)

\[ A = C P_{O_2}^{+1/4} \] (11)

and solving for the respective partial pressures.

One may readily demonstrate that expressions for \( P_n \) and \( P_p \) are given by(10)

\[ \ln P_n = -4\left[ (E_n-E_i)/k \right] /T + 4 \ln (\sigma_{n0}/\sigma_{i0}) \] (12)

\[ \ln P_p = -4\left[ (E_i-E_p)/k \right] /T + 4 \ln (\sigma_{i0}/\sigma_{p0}) \] (13)

where \( E_i, E_n \) and \( E_p \) are the activation energies for the ionic, n-type and p-type partial conductivities, respectively, and \( \sigma_{i0}, \sigma_{h0}, \) and \( \sigma_{p0} \) are the corresponding pre-exponential terms in \( A, B, \) and \( C, \) respectively. The region in \( \ln P_{O_2} \) vs. \( 1/T \) space bounded by Equations 12 and 13, represents the ionic domain within which the ionic transference number remains equal to or greater than 1/2.

3. EXPERIMENTAL

Powder samples were prepared by the "liquid-mix" technique\(^{(20)}\) which enables close control of the cation
stoichiometries. Powders were dry pressed at 10Kpsi, isopressed at 40Kpsi, and then sintered at 1600°C for 16 hours.

Electrical measurements were performed with an HP4192a impedance analyzer operating between 5Hz and 13MHz which enabled the separation of the bulk conductance from the grain boundary and electrode contributions. Similar results were obtained from disc (12 mm dia, x2 mm) and bar (2x3x12 mm³) geometries. Oxygen partial pressures (1-10⁻² atm) were controlled by use of either O₂/Ar or CO/CO₂ gas mixtures and monitored with a stabilized ZrO₂ concentration cell. A more detailed description of experimental techniques may be found in Ref. (15).

4. RESULTS

The isothermal P₀₂ dependence of the electrical conductivity of Gd₂(Zr₀.₄Ti₀.₆)₂O₇ shown in Fig. 3. These data were found to fit well to Equation (9) outside of several points at the highest temperatures and lowest P₀₂'s. It is obvious from Fig. 3 that, at 700°C, the total conductivity is nearly ionic, while at 1400°C, it is nearly entirely n-type electronic. Pₐ and Pₜ were readily determined at each temperature with the assistance of Eq's. (10 and 11) and are shown plotted in Fig. 4. As is the case for stabilized ZrO₂,(10) the ionic domain is observed to shrink rapidly with increasing temperature. The rapid shrinkage of the domain with temperatures under reducing conditions is a consequence of Eₐ = 3.0eV >> Eₐ = 0.82eV while the weak dependence of the other domain boundary is a result of Eₐ = 1.0eV ≒ Eₐ = 0.82eV (see Eq's. 12 and 13).

If we examine the corresponding isothermal conductivity of the x=0.6 composition, i.e. Gd₂(Zr₀.₄Ti₀.₆)₂O₇ shown in Fig. 5, we see that the ionic component of the conductivity now dominates at all but the highest temperatures and lowest P₀₂ values. This is a consequence of two factors. First, as discussed above, the ionic conductivity increases sharply with increasing x, owing to a systematic disordering of the oxygen sublattice. Second, we find(18) that the electronic component of the conductivity drops orders of magnitude with x over the same range of x (0.3 < x < 0.6) which, we believe, is due to a narrowing of the Ti 3d-like conduction band and an increase in the reduction enthalpy, ΔHᵣ, as titanium is replaced by zirconium.

The increase in ionic and decrease in electronic conductivity with increasing x is reflected in a systematic shift of the electrolytic boundary Pₐ towards lower P₀₂ with
increasing zirconium content, as illustrated in Fig. 6. The fact that the boundaries remain parallel is due to the fact that $E_i$ and $E_n$ remain relatively independent of $x$. For Gd$_2$Zr$_2$O$_7$, we find no evidence of electronic conductivity over the ranges of $P_{O_2}$ and temperature that we have examined.

In Fig. 7, we plot the ionic conductivity of Gd$_2$Zr$_2$O$_7$ versus reciprocal temperature and compare it with that of yttria stabilized zirconia (Zr$_{0.91}$Y$_{0.09}$)O$_2$. (22) The ionic conductivity of the pyrochlore is clearly somewhat smaller than stabilized zirconia with the difference decreasing at lower T due to the lower activation energy of the pyrochlore (0.84 eV versus 0.9-1.0 eV).

5. DISCUSSION

The two key criteria that a solid oxide electrolyte must satisfy, namely high oxygen ion conductivity and low electronic conductivity, are satisfied by compositions in the GZT system with high values of $x$. The ionic conductivity of Gd$_2$Zr$_2$O$_7$ is high, e.g. $\approx 2 \times 10^{-2}$ S/cm at 1000°C, which is approximately 1/5 of yttria stabilized zirconia. The activation energy of $\approx 0.84$ eV is approximately 0.10-0.15 eV lower than that of stabilized zirconia. The ionic domain as illustrated in Fig. 6 is already quite broad for GZT with $x=0.6$, e.g. $P_n = 10^{-21}$ atm at 1000°C and we estimate $P_n = 10^{-32}$ atm for $x=1.0$ based upon our observed increase in $\sigma_{\text{ion}}$ with $x$ and an extrapolated decrease in $\sigma_{\text{electron}}$ between $x=0.6$ and 1.0. (18) This compares favorably with $P_n$ values estimated for stabilized zirconia.

Although somewhat lower in ionic conductivity, the GZT system exhibits a number of characteristics which make it an attractive candidate vis-a-vis stabilized zirconia. Since GZT with large values of $x$ is an intrinsic fast ion conductor, it requires no dopants. Further, since the pyrochlore phase is the equilibrium phase, no long term aging affects are expected, as are found for "stabilized" zirconia (21) and $\alpha$-Ta$_2$O$_5$. (8)

Perhaps what is most interesting about the GZT system is its flexibility. By controlling $x$, its lattice parameter may be varied from $\approx 10.18$ at $x=0$ to $\approx 10.53$ at $x=1$. This can be advantageous in lattice matching with substrate or electrode material, thereby reducing strain. Furthermore, the ratio of $\sigma_{\text{ion}} / \sigma_{\text{electron}}$ can be controlled over a wide spectrum by varying $x$ and/or doping which can be of
significant importance in modifying surface regions in order to enhance oxygen exchange rates leading to lower electrode polarization.

Further work is required to determine whether these attributes can overcome GZT's somewhat lower ionic conductivities.

6. ACKNOWLEDGEMENTS

The authors wish to thank the Basic Science Division, U.S. Department of Energy, for their generous support under contract DE-FG02-86ER45261.

7. REFERENCES

1. H. Obayashi and T. Kudo in Solid State Chemistry of Energy Conversion and Storage, Eds. J.B. Goodenough and M.S. Wittingham, American Chemical Society, Washington, DC, 1977, p. 316.

2. O. Antonsen, W. Baukal, W. Fischer, Brown Boveri Rev., 53 21 (1966).

3. T.L. Markin, R.J. Bones, R.M. Dell in Superionic Conductors, Eds. G.D. Mahan and W.L. Roth, Plenum Press, New York, 1976, p.15.

4. T. Takahashi and H. Iwahara, Mat. Res. Bull., 13 1447 (1978).

5. H.L. Tuller and A.S. Nowick, J. Electrochem Soc., 122 255 (1975).

6. T. Kudo and H. Obayashi, J. Electrochem. Soc., 123 415 (1976).

7. A.E. McHale and H.L. Tuller, Solid State Ionics, 5 515 (1984).

8. G.M. Choi, H.L. Tuller, and J.S. Haggerty, J. Electrochem. Soc., 136 835 (1989).

9. H.L. Tuller and P.K. Moon, Mat. Sci. and Eng., B1 171 (1988).

10. H.L. Tuller in Non-Stoichiometric Oxides, Ed. O.T. Sorensen, Academic Press, New York, 1981, p. 271.

11. R.A. McCauley, J. Appl. Phys., 51 290 (1980).
12. P.K. Moon and H.L. Tuller in *Proc. Symp. Solid State Ionics*, Materials Research Society Fall meeting, November 28-December 2, 1988, Boston, MA, in press.

13. T. Van Dijk, K.J. de Vries, and A.J. Burggraaf, *Phys. Stat. Sol. (b)*, 101 765 (1980).

14. T. Van Dijk, K.J. de Vries, and A.J. Burggraaf, *Phys. Stat. Sol. (a)*, 58 115 (1980).

15. P.K. Moon, PhD Thesis, Massachusetts Institute of Technology, Cambridge, MA, 1988.

16. T. Fournier, J.Y. Nots, J. Muller, and J.C. Joubert, *Solid State Ionics*, 15 71 (1985).

17. K. Uematsu, S. Shinuzaki, O. Sakurai, N. Mizutani, and M. Kato, *J. Am. Ceram. Soc.*, 62 219 (1979).

18. P.K. Moon, M.A. Spears, and H.L. Tuller in *Proc. Symp. Char. Struct. Chem. Defects. Mat.*, Materials Research Society, Fall Meeting, November 28-December 2, 1988, Boston, MA, in press.

19. P.K. Moon and H.L. Tuller, *Solid State Ionics*, 28-30 470 (1988).

20. M.P. Pechini, U.S. Patent 3,330,697 (11 July 1967).

21. M. Kleitz, H. Bernard, E. Fernandez and E. Schouler, *Adv. Cer.*, 3 310 (1981).

22. E.C. Subbarao (ed.), *Solid Electrolytes and Their Applications*, Plenum Press, New York, 1980.
Fig. 1: A (100) projection of a portion of one unit cell of the pyrochlore structure.

Fig. 2: Log $\sigma$ vs. mole fraction of zirconium in Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$ at 600°C, 800°C, and 1000°C. The sharp rise in ionic conductivity for $x > 0.2$ should be noted.

Fig. 3: Log $\sigma$ vs. log $P_{O_2}$ for Gd$_2$(Zr$_{0.4}$Ti$_{0.6}$)$_2$O$_7$. ($^{15}$)

Fig. 4: The extent of the electrolytic zone for Gd$_2$(Zr$_{0.4}$Ti$_{0.6}$)$_2$O$_7$ as a function of inverse temperature (from Ref. 9).
Fig. 5: Log $\sigma$ vs. log $P_{O_2}$ for $Gd_2(Zr_{x}Ti_{1-x})_2O_7$ ($x=0.60$).

Fig. 6: The extent of the electrolytic zone under reducing conditions as a function of the composition of $Gd_2(Zr_xTi_{1-x})_2O_7$ (from Ref. 9).

Fig. 7: A comparison of the temperature dependent conductivities of $Gd_2Zr_2O_7$ and $(Y_{0.09}Zr_{0.91})_2O_2$ ($* = YSZ; + = CZ$).