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Praseodymium doped ceria: Model mixed ionic electronic conductor with coupled electrical, optical, mechanical and chemical properties

H.L. Tuller [a,*], S.R. Bishop [a,1], D. Chen [a], Y. Kuru [a,b,2], J.-J. Kim [a], T.S. Stefanik [a,3]

[a] Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA
[b] Department of Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

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ABSTRACT

Praseodymium doped ceria, $Pr_xCe_{1-x}O_{2-\delta}$ (PCO), exhibits many interesting and unusual properties including a pO_2 dependent ionic conductivity, an anomalously large thermal expansion coefficient in air, and a significant electronic conductivity component at elevated pO_2. These unusual features are discussed in terms of the variable valent nature of Pr at elevated pO_2, its position within the ceria band gap and the creation of an impurity band supporting small polaron transport. Implications for use of PCO as a ceria solid electrolyte compatible cathode, stress induced chemical expansion and optically detected redox kinetics are analyzed and discussed.

1. Introduction

The fluorite structured oxide, cerium dioxide (CeO_2) or ceria, is of continuing interest in the solid oxide fuel cell (SOFC) field given its exceptionally high ionic conductivity when doped with lower valent cations such as Gd or Sm [1,2] and as the oxygen storage material in automotive three way catalysts, given its extensive oxygen nonstoichiometry [3]. This latter feature limits the use of acceptor doped ceria as a solid electrolyte at elevated temperatures, since the loss of oxygen at the anode side of the fuel cell is accompanied by the introduction of electronic conductivity as Ce^{4+} is reduced to Ce^{3+}. A less well known feature is the interesting coupling between oxygen loss and lattice dilation. If not properly accounted for, it can lead to stress and then to mechanical failure [4]. In this article, a different variant of ceria is introduced, praseodymium doped ceria, $Pr_xCe_{1-x}O_{2-\delta}$ (PCO), which exhibits many interesting and unusual properties including (1) an oxygen partial pressure (pO_2) dependent ionic conductivity, (2) an anomalously large thermal expansion coefficient in air, and (3) a significant electronic conductivity component not found in either the O 2p derived valence band or the Ce 4f derived conduction band. These unusual features come about as a result of the variable valent nature of Pr at elevated pO_2 (e.g. air). This makes it particularly convenient to study the above phenomena at readily accessible pO_2 and temperatures and, furthermore, makes this ceria variant of interest as a ceria solid electrolyte compatible cathode material.[4]

2. Atmosphere dependent ionic conductivity

The ionic conductivity in most conventional solid oxide electrolytes such as yttria stabilized zirconia (YSZ), gadolinia doped ceria (GDC) or double acceptor doped lanthanum gallate (LSGM) results from the positively charged oxygen vacancies formed in response to the addition of the negatively charged acceptor impurities. The concentration of vacancies is fixed, as is the charge and concentration of the lower valent ions. For example, in GDC

$$\left[Gd'_{Ce}\right] = 2\left[V_O^{\bullet\bullet}\right] \tag{1}$$

The oxygen vacancy concentration formed in this manner is far in excess of those formed due to the reduction reaction:

$$O_O^{\times} \leftrightarrow V_O^{\bullet\bullet} + 2e' + 1/2O_2(g) \tag{2}$$

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* Corresponding author. Tel.: +1 617 253 6890.
E-mail address: tuller@mit.edu (H.L. Tuller).

[1] Current address: International Institute for Carbon Neutral Energy Research (WPI-I^{2}CNER), Kyushu University, Nishi-ku Fukuoka 819-0395, Japan.

[2] Present address: Department of Materials Science and Engineering, Akdeniz University, Dumlupinar Bulvari Kampus, Antalya, 07058, Turkey.

[3] Current address: Nanocerox, Ann Arbor, MI 48108, USA.

[4] This paper is dedicated to Professor John Kilner of Imperial College, London, on the occasion of his 65th birthday and is most appropriate given his long standing interest in the ceria materials system and his contributions to its technological development.

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Therefore, the oxygen vacancy concentration is virtually independent of pO_2, except for the most extremely reducing conditions at elevated temperatures. The same is true for PCO at intermediate pO_2 at which the total Pr concentration $[Pr_{Ce}^{total}]$ is reduced and trivalent, and thus acts like a standard acceptor dopant, like fixed valent Gd or Sm. Like Eq. (1), this fixes the oxygen vacancy concentration as described by:

$$\left[Pr'_{Ce}\right] \approx 2\left[V_O^{\bullet\bullet}\right] \tag{3}$$

thereby leading to predominantly ionic conductivity independent of pO_2. However, as pO_2 is increased, the Pr begins to oxidize to the 4+ oxidation state, which is isovalent with the Ce host ion, thereby leading to a corresponding decrease in oxygen vacancies. At high pO_2, the electrical conductivity and the thermogravimetric behavior, as demonstrated below, are found to be consistent with the following reaction.

$$2Pr_{Ce}^{\times} + O_O^{\times} \leftrightarrow 2Pr'_{Ce} + V_O^{\bullet\bullet} + 1/2O_2(g) \tag{4}$$

with a corresponding mass action law given by

$$\frac{\left[Pr'_{Ce}\right]^2\left[V_O^{\bullet\bullet}\right]}{\left[Pr_{Ce}^{\times}\right]^2\left[O_O^{\times}\right]}P_{O_2}^{1/2} = K_{\circ}\exp\left(\frac{-\Delta H}{kT}\right). \tag{5}$$

For sufficiently high pO_2, most of the Pr takes on the +4 state and so

$$\left[Pr_{Ce}^{x}\right] \cong \left[Pr_{Ce}^{total}\right] \tag{6}$$

which gives the following expression for the oxygen vacancy concentration:

$$\left[V_O^{\bullet\bullet}\right] = \left[Pr_{Ce}^{total}\right]^{2/3}\left[O_O^{\times}\right]^{1/3}K_o^{1/3}\exp\left(\frac{-\Delta H}{3kT}\right)P_{O_2}^{-1/6} \tag{7}$$

This predicts that the oxygen vacancy concentration, and therefore the ionic conductivity, should exhibit a power law dependence on pO_2 with a −1/6 slope in high pO_2. This transition from pO_2 independence at intermediate pO_2 to a decreasing oxygen vacancy concentration with increasing pO_2 is illustrated in Fig. 1, which shows the dependence of the oxygen nonstoichiometry (δ) as a function of pO_2 at 650 °C.

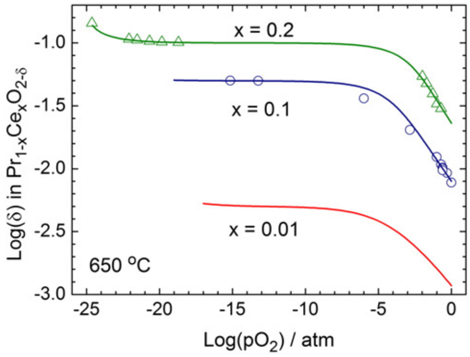

Fig. 1. Non-stoichiometry for three compositions of $Pr_xCe_{1-x}O_{2-\delta}$. Experimentally derived values (symbols) for x = 0.2 are from [16] and x = 0.1 are from [6]. Solid lines are from a defect equilibrium model developed in [6].

3. Mixed ionic and electronic conductivity under oxidizing conditions

It is interesting to note that the reduction reaction described by Eq. (4) contains no explicit electrons, in contrast to the reduction reaction described by Eq. (2). This follows from the fact that while the electrons released by the reduction reaction in Eq. (2) end up in the conduction band of ceria (increasing the concentration of Ce^{3+}), the electrons released by the reduction reaction in Eq. (4) instead end up localized and trapped on the Pr ion (increasing the concentration of Pr^{3+}), whose energy level lies within the ceria band gap, as illustrated in Fig. 2.

At low concentrations of Pr, these levels are nearly discrete and thus no measurable conduction along these levels is expected or observed. As the Pr concentration increases, wave function overlap between adjacent Pr ions leads to broadening of the discrete levels into *impurity* bands with potential to support carrier hopping from one atom to the next. This small polaron hopping, however, also requires that the Pr be mixed valent, given that electrons on Pr^{3+} sites can only hop to an adjacent Pr site if it is empty, e.g. in the Pr^{4+} state. Thus the small polaron contribution to the electronic conductivity is proportional to the product of $[Pr'_{Ce}][Pr_{Ce}^{x}]$ leading, ideally, to a maximum as a function of pO_2 at the point where the concentrations of the two valence states are equal. Indeed, at high pO_2 the conductivity data for $Pr_xCe_{1-x}O_{2-\delta}$ for x = 0.2 in Fig. 3 illustrates this feature, while PCO with low concentrations of Pr do not. In intermediate pO_2, PCO with x = 0.2 has a lower pO_2 independent ionic conductivity than PCO with x = 0.1, consistent with other observations showing that defect association at high dopant acceptor levels leads to corresponding reductions in ionic conductivity [5].

With models available to predict the magnitudes of both ionic and electronic conductivities as functions of temperature, pO_2, and x in PCO [6,7], it becomes possible to map out the ionic transference number, t_{ion}, as a function of these parameters, as illustrated in Fig. 4. Transference numbers close to 0.5 are optimum for supporting rapid redox kinetics given that the oxygen chemical diffusivity is maximum at this point [8]. Since Pr serves to introduce electronic conductivity at higher pO_2, this leads to ionic transference numbers less than unity, a desirable feature for cathode materials as discussed below. Interestingly, at very low pO_2, t_{ion} is observed to reach a maximum at x = 0.1. This comes about because the oxygen vacancy concentration is higher than for x = 0.01, while the enthalpy of ion migration at x = 0.1 is lower than for x = 0.2.

4. PCO as a cathode material

The MIEC behavior of PCO at high pO_2 presents an opportunity for its implementation in SOFC cathodes, where mixed conductivity is known to enhance oxygen surface exchange kinetics [9]. Impedance measurements performed on thin film PCO electrodes deposited onto yttria-stabilized zirconia with varying geometries, and reported elsewhere [10], demonstrate that the electrode performance, dominated by oxygen surface exchange kinetics, compares favorably with that of several high performance cathode materials (e.g. LSF) as illustrated in Fig. 5. This demonstrates the potential of using PCO as a compatible cathode material to ceria based electrolytes, given its identical fluorite structure, good lattice match, and similar chemistry.

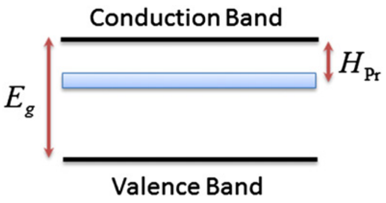

Fig. 2. Schematic of Pr impurity band located within the gap between the conduction (C.B.) and valence (V.B.) bands of ceria defined in [6].