Electrical conducting properties of rare earth doped perovskites

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Abstract

Rare earth doped pervoskites, such as Yb–SrCeO$_3$, show remarkable electrical conducting properties, depending upon the temperature and the surrounding gaseous atmosphere. These materials are well known for their protonic conduction within a certain intermediate temperature range, provided they are subjected to an atmosphere containing sufficient amounts of hydrogen or water vapour. At a temperature, which is relatively lower, in an atmosphere containing water vapour and sufficient oxygen, these perovskites acquire hydroxyl ionic conduction. At elevated temperatures when the partial pressure of oxygen is very low, even in the presence of hydrogen and/or water vapour, the mode of conduction is purely by oxygen ions. On the other hand, when the partial pressure of hydrogen is low but that of oxygen is high, electronic conduction is observed. Experimental results to demonstrate the various modes of conduction, including mixed mode conductions at the boundaries are presented.
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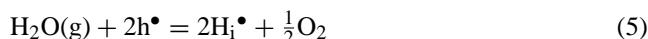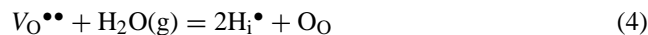*Keywords:* Perovskites; Ionic conductors; Rare earths; Mixed conductors

1. Introduction

Undoped perovskites such as SrCeO$_3$ or BaCeO$_3$ are normally low-conductivity electronic semi-conductors and when doped with aliovalent cations of rare earth elements such as Gd(III), Nd(III) or Yb(III) [1–3] acquire oxide ion vacancies. These vacancies form directly as a result of the replacement of Ce by RE(III) ions (where RE represents rare earths) in the B sites of the perovskite ABO$_3$, where the maximum concentration of oxygen vacancy is given by:

$$[V_O^{\bullet\bullet}] = \frac{1}{2}[\text{RE(III)}] \tag{1}$$

The presence of vacant oxide ions has been shown to be responsible for extensive protonic conductivity at elevated temperatures in these materials in presence of H$_2$ or H$_2$O arising by the following mechanism [4]:In hydrogen:

$$V_O^{\bullet\bullet} + \tfrac{1}{2}O_2(g) = 2h^\bullet + O_O \tag{2}$$

$$H_2(g) + 2h^\bullet = 2H_i^\bullet \tag{3}$$

In water vapour:

$$V_O^{\bullet\bullet} + H_2O(g) = 2H_i^\bullet + O_O \tag{4}$$

$$H_2O(g) + 2h^\bullet = 2H_i^\bullet + \tfrac{1}{2}O_2 \tag{5}$$

It has been suggested that the interstitial proton is strongly associated with a neighbouring oxygen ion and thus the hydrogen interstitial can also be represented as (OH)$^\bullet$ [5,6]. Proton conductivity is explained by a hopping mechanism whereby the protons migrate from one oxygen ion to another nearest oxygen ion. In addition to protonic conductivity a topic, which is widely investigated and reported [4], these materials can also exhibit other modes of conductivity such as electronic, oxygen and hydroxyl transport.

2. Protonic conductivity

Most of the investigations and applications related to the rare earth doped perovskites have been concerned with the presence of protonic conductivity and these results have been reviewed by Kumar and Iwahara [4] and some relevant results are summarised here. It is reported that in the temperature

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range 673–1073 K, presence of water vapour introduced protonic conduction in these materials by a process of dissolution of water vapour. For example with $SrCeO_3$ doped with 5 mol% of Yb, the activation energy for protonic conduction is ~0.55 eV with a typical value of conductivity given as ~6×10^{-3} S cm^{-1} at 1000 K. At a given value of p_{H_2O}, protonic conduction is independent of the partial pressure of oxygen (p_{O_2}) provided p_{O_2} is above a critical value [7]. Under these conditions, the following equation must hold:

$$[H_i^\bullet] + 2[V_O^{\bullet\bullet}] = [RE_{Ce}']$$ (6)

Accordingly it follows that at very low values of p_{O_2} as long as it is below a critical value, the extrinsically created oxide ion vacancies are not fully saturated with oxygen atoms and the above equality (Eq. (6)) does not hold. Reaction (2) suggests that the hole conductivity should decrease with decreasing values of p_{O_2} at a given temperature. This is clearly demonstrated in the paper reported by Uchida et al. [7]. They also reported that the total conductivity also decreased with decreasing p_{O_2} values. Furthermore in a previous paper, Iwahara et al. [1] suggested that the material could behave as a mixed proton–hole conductor when the value of p_{O_2} is increased.

In our study, it was found that for $SrCeO_3$ doped with 5 mol% of Yb, the protonic domain was stable in presence of water vapour over a wide range of p_{O_2} values depending upon the temperature provided temperature was >700 K. As shown in Fig. 1, emf at 36 mV at a selected temperature of 773 K, was independent of p_{O_2} (10^{-6} to 1 atm) for steam concentration cells using water vapour pressures of 0.073 ($p_{H_2O^I}$) and 0.023 ($p_{H_2O^{II}}$) atm, at the two electrodes respectively, represented by the cell:

$$H_2O^I/O_2, Pt|SrCeO_3(5 \text{ mol\% of Yb})|Pt, H_2O^{II}/O_2 \quad \text{(cell I)}$$
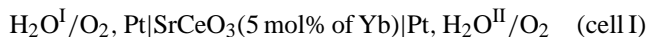
The theoretically expected emf can be calculated assuming purely protonic conduction for the doped perovskite, using the Nernst expression:

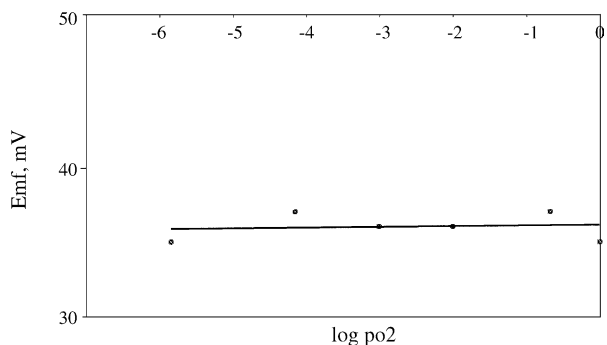$$\text{emf} = \left\{ \frac{RT}{4F} \right\} \ln \left(\frac{p_{H_2O^I}}{p_{H_2O^{II}}} \right)$$ (7)

Fig. 1. Emf vs. partial pressure of oxygen for a humidity concentration cell.

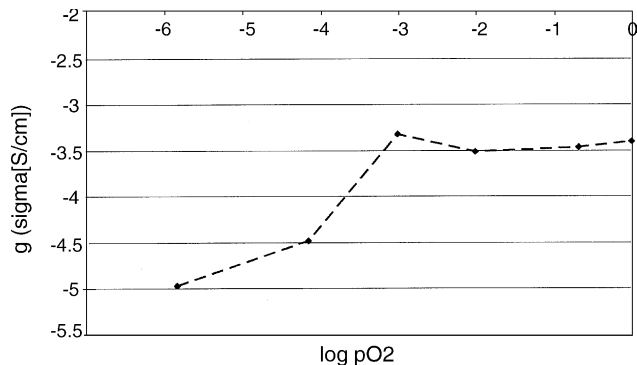Fig. 2. Total conductivity vs. partial pressure of oxygen at $p_{H_2O} = 0.073$ atm ($T = 773$ K).

For the steam concentration cell I at 773 K, the calculated emf is 38 mV which is in good agreement with the measured value of 36 mV confirming the assumption of protonic conduction under the experimental conditions.

In Fig. 2, it can be seen that the conductivity of $SrCeO_3$ (5 mol% of Yb) at a water pressure of 0.073 atm is independent of the partial pressure of oxygen at 773 K and at a value of $p_{O_2} > 10^3$ atm, whereas it begins to decrease at lower values of oxygen partial pressure. Although the conductivity decreases the emf data in Fig. 1, clearly indicate that the protonic domain is unaffected in the range of p_{O_2} values investigated. The presence of mixed hole–protonic conduction could not be readily detected by varying the oxygen pressures using the above cell.

3. Hole conduction

Conditions for promoting hole type of conductivity can be rationalised by examining reactions (1) and (2), according to which semi-conduction can be promoted by (i) very low levels of p_{H_2} or p_{H_2O} (ii) high temperature and (iii) high p_{O_2}. Decrease in the transport number for protons accompanied by an increase in electronic conductivity has been demonstrated and reported in the literature for conditions of low p_{H_2} or p_{H_2O} and high temperatures [1–4,7,8]. The effect of temperature has been investigated using impedance spectroscopy in the temperature range 450–1100 K under H_2O/air, by measuring the total conductivity and any activation energy changes, which may represent changes in the mode of conduction [9]. Activation energy data is given for $SrCeO_3$ (5 mol% of Yb) in Table 1, for a p_{H_2O} value of 0.023 atm in air. In the temperature range from 623 to 1050 K, both the conductivity data and the activation energy values are in general agreement

Table 1
Activation energy from conductivity data [9] for $SrCeO_3$ (5 mol% of Yb)

Temperature range (K)	Activation energy (eV)
450–600	0.43
600–1073	0.55
1073–1273	0.88

Table 2
Comparison of activation energy for protonic conduction in SrCeO$_3$ (5 mol% of Yb)

Atmosphere	Temperature (K)	Activation energy (eV)	Reference
H$_2$O/air	623–1053	0.55	[9]
Air	473–873	0.65	[10]
H$_2$O/air	873–1273	0.62	[11]
H$_2$O/nitrogen	500–1273	0.55	[12]
Air	773–1073	0.57	[12]

with other reported data in the literature for the protonic conductivity [10–12], The activation energy data comparison is shown in Table 2.

At temperatures greater than 1073 K, the activation energy is increased to 0.88 eV, a value which is comparable to the range 0.7–0.9 eV reported in the literature for several ceria based oxide ion conductors [13]. Therefore, Kumar et al. ascribed this region as representing a shift to oxide ion domain in their earlier paper [9], subsequent work has shown that an oxygen concentration cell with this electrolyte under the above conditions report an emf of zero, indicative of electronic conductivity [8]. Thus, the activation energy of 0.88 eV is ascribed to hole conduction. Kurita et al. [14] reported that for CaZrO$_3$ doped with 10 mol% In$_2$O$_3$ the activation energy is 0.74 eV for protonic conduction, 2.5 eV for oxide ion conduction and 1.21 eV for hole conduction. It is concluded that the observed activation energy of 0.88 eV for SrCeO$_3$ (5 mol% of Yb) at $T > 1073$ K is more likely to be for holes rather than oxide ions. Given the availability of several modes of electrical transport regimes in these materials, an unambiguous association of activation energy to the operating mode of conductivity is important for characterising the material.

4. Oxygen-ion conduction

Kurita et al. [14] deduced the presence of and shift to oxygen ionic domain for CaZrO$_3$ doped with 5 mol% In$_2$O$_3$ by measuring the total conductivity under varying conditions of temperature and partial pressures of hydrogen, water vapour and oxygen by noting the changes in activation energies. The above work is an important contribution for clearly describing the presence of oxygen ion conduction in these doped perovskites, oxygen concentration cells based upon these materials producing emfs according to Nernst equation have not yet been demonstrated in the literature.

From reaction (2) it follows that at a given temperature (preferably high) and at a given p_{H_2}, there is a critical value of p_{O_2} below which oxide ion vacancies are stable and not exchanged for holes or protons. In order to observe pure oxygen ionic conduction very high temperatures may be required given the very high value of activation energy (2.5 eV) reported by Kurita et al. [14]. Furthermore, it is important to set up very low levels of oxygen pressures at the two electrodes.

To demonstrate the principle of pure oxygen ion conduction, even in the presence of hydrogen, the following cell was constructed [15]:

Pt, $p_{H_2} = 0.01$ atm, Ta, Ta$_2$O$_5$,

|RE doped perovskite|Cr, Cr$_2$O$_3$, $p_{H_2} = 0.01$ atm, Pt

(cell II)

The above cell II is constructed as a sandwich type of system, which is subject to flow of hydrogen gas at a partial pressure of 0.01 atm such that both electrodes are at uniform hydrogen potential. The hydrogen gas if dehydrated to very low levels of water vapour beyond the detection of humidity meters in order to minimise interference of oxygen pressures from H$_2$/H$_2$O equilibrium. Despite dehydration, the p_{O_2} associated with the gas phase is oxidising to both Ta and Cr. Excess amounts of Ta and Cr are used so that some inevitable oxidation at the gas/electrode interface does not affect the oxygen partial pressure in the solid composite electrode systems. The sandwich system is spring-loaded in order to ensure good interfacial contact at the two-electrode/electrolyte interfaces such that the low p_{O_2} values can be maintained for long periods of time.

The emf results at a selected temperature of 1273 K for the above cell as a function of time are shown in Fig. 3 [15] and compared with the calculated value from the Nernst equation:

$$emf = -\left[\frac{RT}{4F}\right] \ln\left\{\frac{p_{O_2}^{Ta/Ta_2O_5}}{p_{O_2}^{Cr,Cr_2O_3}}\right\} \tag{8}$$

The results as shown in Fig. 3, strongly suggest the presence of pure oxygen ionic conduction and also from the observation of stable non-zero emf, one can rule out the possibility of protonic or hole conduction under these operating conditions. At $T > 1200$ K, the experimental emf is in good agreement with the Nernstian emf calculated for pure oxygen ion conduction, as shown in Fig. 4 by data points pertaining to experiment 2. If the temperature is decreased below 1200 K,
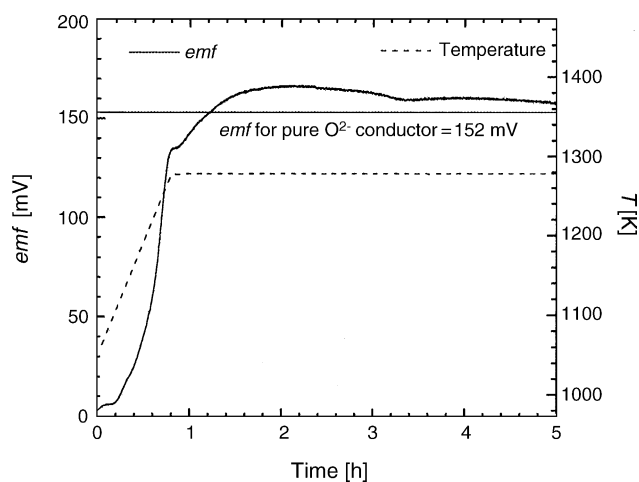

Fig. 3. Emf vs. time of the oxygen concentration cell at 1273 K at $p_{H_2} = 0.01$ atm Ta, Ta$_2$O$_5$ |GaZrO$_3$ (In doped)| Cr, Cr$_2$O$_3$.
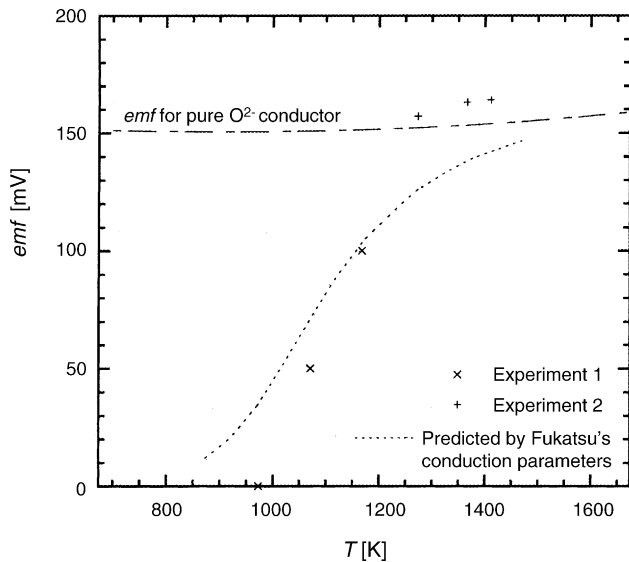
Fig. 4. Emf vs. temperature for the oxygen concentration cell at $p_{H_2} = 0.01$ atm Ta, Ta$_2$O$_5$ |CaZrO$_3$ (In doped)| Cr, Cr$_2$O$_3$.

the emf values depart from the Nernst equation calculated emfs for the oxygen concentration cell and achieve a value of zero at 900 K (Fig. 4, experiment 1) [15]. At a temperature below 900 K, the material reverts to full protonic conduction, while in the range 900–1200 K the domain is considered to be by a mixed proton-oxide ion conduction mechanism under the operating conditions defined by relatively low values of oxygen partial pressures.

The above galvanic cell was also used for measuring the total conductivity using impedance spectroscopy. Bulk conductivity was deduced from Nyquist plots and shown in Fig. 5 [15]. Based on the assumption that the electrolyte is in the oxygen domain at $T > 1200$ K, the activation energy for
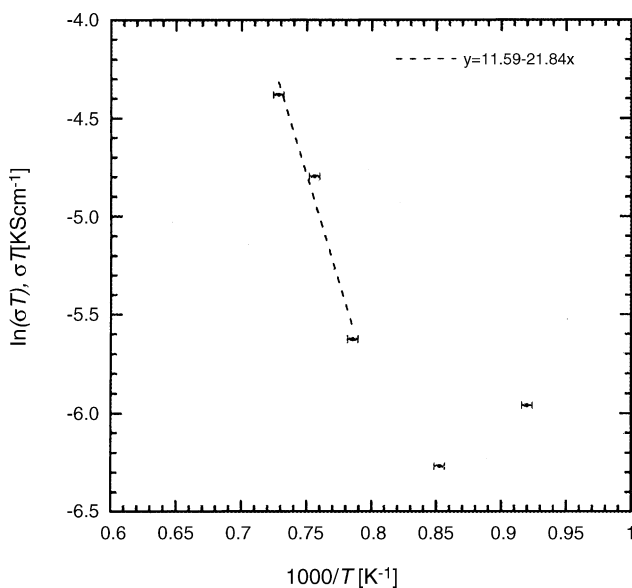

Fig. 5. Arrhenius plot for the oxygen concentration cell at $p_{H_2} = 0.01$ atm Ta, Ta$_2$O$_5$ |CaZrO$_3$ (In doped)| Cr, Cr$_2$O$_3$.

Table 3
The emf of steam concentration cell in air with SrCeO$_3$ (5 mol% of Yb) electrolyte and p_{H_2O} varying from 0.023 to 0.073 atm

Temperature (K)	Emf (measured; mV)	Emf (calculated; mV)	Remarks
500	−28	−25	OH$^+$ conduction
573	−27	−28	OH$^-$ conduction
623	20	−31 (for OH$^-$ conduction) and 31 (for H$^+$ conduction)	Transition form OH$^-$ to H$^+$ conduction
700	27	−34 (for OH$^-$ conduction) and +34 (for H$^+$ conduction)	Mixed OH$^-$ and H$^+$ conduction
773	36	38	H$^+$ conduction

oxygen ion conduction in indium doped CaZrO$_3$ has been measured as 1.73 eV which is lower than the 2.5 eV reported by Kurita et al. [14]. These experiments provide a convincing demonstration of oxygen ion domain at low partial pressures of oxygen and suggest that at elevated temperatures oxygen vacancies are stabilized in the material. The activation energy reported in this work is based on direct measurement during pure oxygen ion conduction.

5. Hydroxyl-ion conduction

The behaviour of the rare earth doped perovskites is considerably different at relatively low temperatures. For example as can be seen in Table 1, for SrCeO$_3$ (5 mol% of Yb) there is a low activation energy regime (of 0.43 eV) at temperature <600 K in the conductivity versus temperature plot in steam/air atmosphere. Kumar et al. [9] ascribed this phenomenon to OH$^-$ (hydroxyl ion) conduction. Shin et al. [16] also reported a change in slope in the Arrhenius plot for doped SrCeO$_3$ and SrZrO$_3$ (both doped with 5 mol% Y) single crystals at 773 K in air/steam atmosphere. At temperatures below 773 K, the activation energy for the SrZrO$_3$ system was observed to be 0.45 eV increasing to 0.54 eV at higher temperatures. Using IR measurements, the authors reported that the low value of activation energy is closely related to the value of the OH binding energy suggesting the presence of hydroxyl groups in the material.

Kumar et al. [9] also reported that the temperature at which the Arrhenius slope exhibits a change corresponds well to the emf measurements, as shown in Table 3 where the polarity of the emf values change sign in steam concentration cell (Cell I) measured in air as the operating temperature is decreased from 773 to 500 K. Nernst emf for pure hydroxyl ion conduction is calculated using the equation:

$$\text{emf} = -\left\{ \frac{RT}{4F} \right\} \ln \left(\frac{p_{H_2O^I}}{p_{H_2O^{II}}} \right) \qquad (9)$$

is opposite in sign in comparison with that for pure protonic conduction as expressed in Eq. (7). The mecha-

nism by which hydroxyl ion conduction is acquired is not clear.

Is it most unlikely that transport of the lattice oxide ions is involved directly given the large activation energy associated with oxygen ion transport. It is speculated, at this stage that given the high solubility of water in these doped perovskites especially at low temperatures, that chemically combined water with a high pH is present in the grain boundary or interfacial regions of the sample giving rise to interfacial conduction of OH^- ions. Such a conduction is likely given the stability of $Ce(OH)_3$ and $Se(OH)_2$ that can form at the grain boundaries at low temperatures and the observation of low activation energy normally associated with interfacial type of transport of ions (OH^- in this case) in solid electrolyte materials.

6. Conclusions

Rare earth doped perovskites exhibit varying modes of conduction ranging from protonic for which it is highly prized, to hydroxyl, oxygen and hole depending upon the atmospheric condition and the temperature, the presence of each of the domain has been experimentally demonstrated.

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