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ON THE MIXED IONIC-ELECTRONIC CONDUCTIVITY IN
Ca-DOPED $\text{La}_2\text{Ti}_2\text{O}_7$

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ABSTRACT

The electrical conductivity of Ca doped $\text{La}_2\text{Ti}_2\text{O}_7$ has been studied by means of ac-impedance spectroscopy and EMF concentration cell measurements with emphasis on effects of protons. The material exhibits n- and p-type conductivity under reducing and oxidizing conditions, respectively. At intermediate oxygen pressures, ionic conductivity predominates with protons and oxygen ions as the major charge carriers below and above $\sim 800^\circ\text{C}$, respectively. From variations of the conductivity with water vapour and oxygen pressures it was concluded that the defect structure is predominated by oxygen vacancies and protons compensating the Ca acceptor. The thermodynamics for the equilibrium between oxygen vacancies and protons and the transport parameters of protons and oxygen ions have been extracted from modelling of the conductivity.

1. INTRODUCTION

High-temperature mixed ionic-electronic conductors find applications in processes related to conversion between chemical energy and electricity, e.g. as electrodes in SOFCs or as gas separation membranes. Whereas oxygen separation membranes based on mixed ionic-electronic conducting materials are on their way into the market, hydrogen separation membranes still exhibit too low permeation or are chemically unstable. There is, as such, a need to develop new and better mixed proton-electron conducting materials.

Permeation of hydrogen through a dense ceramic membrane is proportional to the ambipolar conductivity, $[(\sigma_H \cdot \sigma_{el}) / \sigma_{tot}]$. High-temperature proton conductors known so far exhibit rather poor electronic conductivity and the overall H₂-flux accordingly becomes low. To ensure an appreciable electronic conduction, candidate materials should contain reducible cations and have a relatively small bandgap. It has been shown in the literature that pyrochlore-structured oxides containing Ti exhibit relatively high mixed oxygen ion-electron conductivities [1-3]. Proton conductivity has been observed in the pyrochlore La₂Zr₂O₇, but has not been reported in isostructural Ti-containing oxides [4, 5]. On the contrary Shimura et al. [6] concluded that Y₂Ti_{1.8}M_{0.2}O_{7-δ} (M=In and Mg) did not show any measurable proton transport. However, on basis of empirical models to predict proton conductivity in oxides, A-site acceptor doped La₂Ti₂O₇ may seem as a better candidate [7]. The conductivity of undoped La₂Ti₂O₇ has previously been measured, but only at relatively high temperatures (800-1000°C) and with no emphasis on possible effects of protons and proton transport [8].

On this basis, the present contribution addresses the mixed proton-oxygen ion-electronic conductivity of 2% Ca-doped La₂Ti₂O₇ to evaluate its potential as a candidate material for gas separation membrane applications. The conductivity has been measured as a function of the oxygen pressure and water vapour pressure in atmospheres ranging from wet H₂ to wet O₂ (2% H₂O) between 300 and 1200°C by ac impedance spectroscopy. The partial conductivities have, furthermore, been determined by the EMF technique. Thermodynamic and mobility parameters are determined from modelling of the conductivity data on basis of the point-defect structure.

2. EXPERIMENTAL

La₂Ti₂O₇ doped with 2% Ca substituting La were synthesized through the solid-state route by co-milling nominal amounts of La₂O₃, TiO₂ and CaCO₃ in an agate planetary ball-mill in isopropanol for 20 minutes. After evaporating the alcohol, the powder mixture was isostatically pressed to pellets. These pellets were calcined at 900°C for 15 hours after which they were crushed down and re-milled. The calcination procedure was repeated (usually three times) until powder-XRD showed that single-phase, Ca-doped La₂Ti₂O₇ was formed. The single-phase powder was again pressed into pellets with a 25 mm die at 6 metric tons and sintered at 1400°C yielding specimens for conductivity measurements with a relative density above 95%.

Circular Pt electrodes (diameter ~1 cm) were attached on both sides of the specimens by first painting one layer with Pt ink, then adding a Pt-net and, finally, painting 2 to 3 layers with the Pt-ink. The electrode assembly was annealed at 1000°C to burn off residual organics from the ink and to ensure that the electrodes had a proper conductivity and adherence to the specimen. Thereafter the specimens were mounted in a ProboStat™ measurement cell [9] on top of the inner support tube (alumina), with a 1 mm thick gold gasket between the tube and the specimen. With the outer, closed

alumina tube in position, this forms two gas-compartments separated by the specimen. Pt-electrode leads, coming from the cold zone inside the support tube and outside (between the support tube and the outer tube) were attached to the electrodes on the specimen itself. A strong spring load ensured proper contact between the electrode leads and the specimen electrodes in addition to improving the sealing. After heating to $\sim 1060^\circ\text{C}$ no leakage was detected between the two chambers (by mass spectrometry). By connecting the cell to a gas mixer, gradients in oxygen and/or hydrogen and/or water vapor could be established across the specimen. Variations in the water vapor pressure under reducing conditions were obtained by diluting wet hydrogen (2% H_2O) with Ar.

The open circuit voltage as a consequence of the gradients across the specimen was measured with a Solartron 7150 multimeter. Total conductivity measurements were performed with a Solartron 1260 FRA impedance analyzer as a function of temperature, oxygen pressure and water vapour pressure. Impedance spectroscopy was applied to deconvolute the total resistance into its different contributions corresponding to bulk, grain boundary and the electrodes.

3. RESULTS

The dependence of the oxygen pressure on the total conductivity of 2% Ca-doped $\text{La}_2\text{Ti}_2\text{O}_7$ at 600, 800, 1000 and 1200°C in wet gases ($p_{\text{H}_2\text{O}}=0.02$ atm) is shown in Fig. 1. The conductivity increases with decreasing oxygen pressure under reducing conditions and with increasing oxygen pressure under oxidizing conditions. These two regimes are separated by a region where the conductivity is independent of the oxygen pressure. For the sake of interpretation, one should note that the total conductivity approaches a $\sigma_{\text{tot}} \propto p(\text{O}_2)^{-1/4}$ dependence at and below $\sim 1000^\circ\text{C}$ whereas the very reducing data for 1200°C appears to follow a $\sigma_{\text{tot}} \propto p(\text{O}_2)^{-1/6}$ dependence.

The total conductivity as a function of the water vapor pressure under reducing conditions is presented in Fig. 2 at different temperatures. At 400 and 600°C the conductivity increases with increasing water vapor pressure. However, at 800 and 1000°C there is essentially no effect of the water vapour.

The different contributions to the total conductivity in wet H_2 as extracted from measurements of the EMF in a concentration cell are shown in Fig. 3. It was shown by impedance spectroscopy that the electrode overpotentials were sufficiently low as compared to the sum of the electronic and ionic volume resistance [$R_{\eta}/(R_{\text{el}}+R_{\text{ionic}})\sim 0.1$] to justify use of the Wagner equation for determination of the ionic transport numbers. Overall, the conductivity is predominated by electronic charge carriers. Protons are the major ionic charge carrier below 800°C above which oxygen ions predominate. The proton conductivity goes through a maximum at 750°C of $\sim 6 \cdot 10^{-5}$ S/cm. At high temperatures under very reducing conditions (wet H_2), one should note from Fig. 3 that an apparently negative hydrogen species contributes to the total conductivity.

Different approaches have been made to interpret this behavior. However, since this phenomenon has been treated in several recent papers, it will not be further discussed within this contribution [10-12].

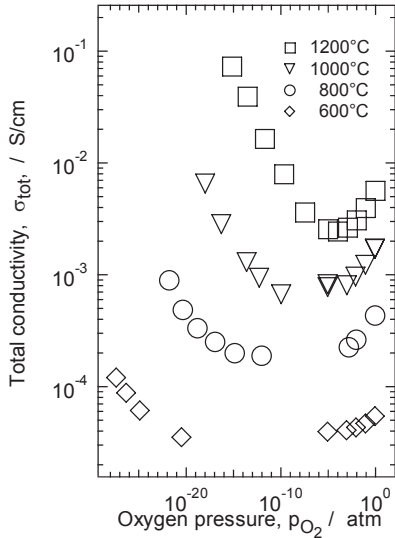


Fig. 1. Total conductivity as a function of the oxygen pressure under wet conditions ($p_{H_2O}=0.02$ atm).

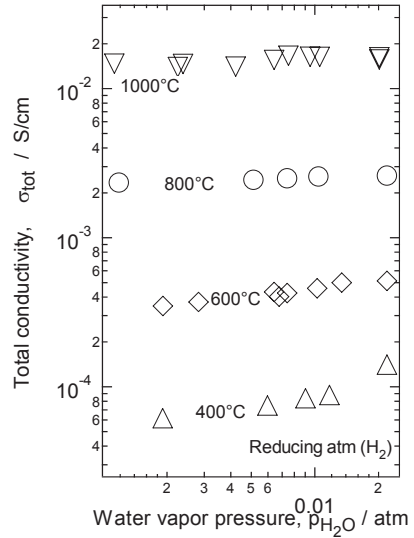


Fig. 2. Total conductivity as a function of p_{H_2O} in H_2+H_2O atmospheres with fixed p_{H_2}/p_{H_2O} ratio.

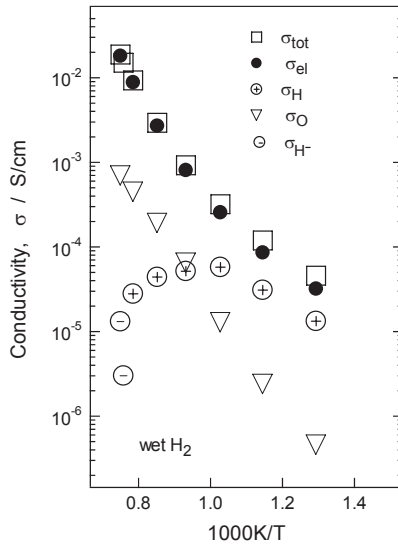


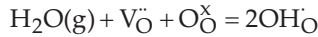
Fig. 3. Partial and total conductivities as function of the inverse absolute temperature under reducing conditions (0.98 atm H_2 , 0.02 atm H_2O).

4. DISCUSSION

The conductivity behaviour of Ca-doped La₂Ti₂O₇ exhibits - depending on the reaction conditions - both ionic and electronic characteristics. On basis of the oxygen pressure dependence in Fig. 1, the conductivity has been concluded to be predominantly n- and p-type electronic under reducing and oxidizing conditions, respectively. At intermediate pressures, the independence on the oxygen pressure suggests that the conductivity is predominantly ionic and that oxygen vacancies and protons charge compensate the acceptor:



The equilibrium between oxygen vacancies and protons in oxides,



has been given much attention in the literature. Since the thermodynamics of this reaction are essential as to whether a material dissolves protons, the enthalpy, ΔH_{hydr} , and entropy, ΔS_{hydr} , of the reaction has been determined from both experimental data (thermogravimetry, conductivity measurements, calorimetry etc.) as well as from a more theoretical approach. With basis in the electroneutrality condition, the approach by Kreuer [13], Larring [14], and Norby et al. [15] has been applied to model ΔH_{hydr} , ΔS_{hydr} and mobility parameters of protons and oxygen ions from the conductivity data of Figs. 1-3. On basis of the empirical finding that the loss of one gas molecule represents an entropy of ~ -120 J/molK and, moreover, that literature values usually falls into the range from -160 to -100, ΔS_{hydr} was restricted in the fitting to the interval -120 \pm 20 J/molK [15]. This resulted in the following set of physicochemical data representing the ionic part of the conductivity: $\Delta S_{\text{hydr}} = -120\pm 20$ J/molK, $\Delta H_{\text{hydr}} = -120\pm 15$ kJ/mol, $\mu_{\text{H}^+,0} = 2.0\pm 1.8$ cm²K/Vs, $\Delta H_{\text{mob,H}^+} = 45\pm 10$ kJ/mol, $\mu_{\text{O}_2^{\cdot-},0} = 10\pm 5$ cm²K/Vs, $\Delta H_{\text{mob,O}_2^{\cdot-}} = 50\pm 5$ kJ/mol.

From the partial conductivities of Fig. 3 and with basis in the present defect situation one may estimate the flux of H₂ across a 10 μm thick Ca-doped La₂Ti₂O₇ film. Since the electronic conductivity is predominating, the maximum flux of H₂ would be obtained under conditions corresponding to the maximum in proton conductivity. If we assume a pressure difference of 10 atm H₂ between the feed and the permeate side, operating

the membrane at 750°C would yield a H₂ flux of the order of 0.1 mL_N/cm²min. Comparing this value with the best mixed electron-proton conducting perovskites, 5% Yb-doped SrCeO₃ would, under corresponding reaction conditions exhibit a H₂-flux of a factor of ~5 higher than La₂Ti₂O₇ [16, 17]. Despite being inferior compared to Yb-doped SrCeO₃ with respect to the H₂ permeation, one should recognize that La₂Ti₂O₇ is one of the very few CO₂ tolerant materials known so far with an appreciable mixed proton-electron conductivity under reducing conditions.

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REFERENCES

1. H.L. Tuller, *Solid State Ionics* 52, 135 (1992).
2. S.A. Kramer and H. Tuller, *Solid State Ionics* 82, 15 (1995).
3. U. Heider, L. Jörissen, R.A. Huggins and W. Witschel, *Ionics* 2, 7 (1996).
4. A. Thurmann Nielsen, Master Thesis, University of Oslo (1996)
5. J.A. Labrincha, J.R. Frade and F.M.B. Marques, *Solid State Ionics* 99, 33 (1997).
6. T. Shimura, M. Komori and H. Iwahara, *Solid State Ionics* 86-88, 689 (1996).
7. R. Glöckner, Ph.D. Thesis, University of Oslo (2000).
8. U. Balachandran, N. G.Eror, *J. Less-Common Met.* 85, 111 (1982).
9. www.norecs.com.
10. S. Steinsvik, Y. Larring and T. Norby, *Solid State Ionics* 143, 103 (2001).
11. M. Widerøe, M. Munch, Y. Larring and T. Norby, *Solid State Ionics*, 154-55, 669 (2002).
12. M. H. Widerøe, Ph.D. Thesis, University of Oslo (2005).
13. K.D. Kreuer, Th. Dippel, Yu. M. Baikov and J.Maier, *State Ionics*, 86-88, 613 (1996).
14. Y. Larring, Ph.D. Thesis, University of Oslo (1998).
15. T. Norby, M. H. Widerøe, R. Glöckner, and Y. Larring, *Dalton Trans.* 19, 3012 (2004).
16. S. Hamakawa, L. Li, A. Li and E. Iglesia, *Solid State Ionics* 148, 71 (2002).
17. R. Haugsrud, unpublished results.