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# Mixed hydrogen ion–electronic conductors for hydrogen permeable membranes

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## Abstract

The potential uses for hydrogen permeable gas separation membranes are introduced, and a simple mixed protonic–electronic conductor theory for calculation of flux rates is given. Example permeations are derived as a function of pressure gradients for different defect models, and the results of the very few available experimental studies of hydrogen permeation through oxides are discussed briefly. Strategies for new candidate materials are outlined. Indications of hydride ion transport in oxides under reducing conditions are introduced, and the behaviour and possible role of hydride defects in oxides is discussed. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Protons; Proton conductivity; Hydride ions; Hydride ion conductivity; Mixed proton conduction; Hydrogen permeation; Gas separation

*Materials:* SrTiO<sub>3</sub>; Nd<sub>2</sub>O<sub>3</sub>; BaCeO<sub>3</sub>; CeO<sub>2</sub>

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## 1. Introduction

After the recent advances in the development of oxygen permeable membranes for production of oxygen from air or production of syngas (CO + H<sub>2</sub>) from methane, there is emerging interest in the possibility of developing mixed protonic–electronic conductors for hydrogen separation [1]. Potential applications comprise extraction of pure hydrogen from syngas or from other oxidation or dehydrogenation steps, as well as hydrogen purification in general. Fig. 1 illustrates how the oxygen permeable and hydrogen permeable membranes in principle

may be used together in a combined process of partial oxidation and hydrogen extraction.

Oxygen permeable membranes operate in a large chemical potential gradient (e.g. syngas production) or in a merely hydrostatic pressure difference under oxidising conditions (oxygen production). Hydrogen permeable membranes, on the other hand, may be foreseen to work mainly in a hydrostatic pressure difference of hydrogen, and thus only under reducing conditions. This has important consequences for the strategies of materials development.

A palladium membrane or a two-phase system of one proton conductor and one electronically conducting (e.g. metallic) phase are alternatives to the mixed conductor. Hydrogen is also well suited for filtering through (nano)porous materials. However, here the topic is that of hydrogen permeability based on

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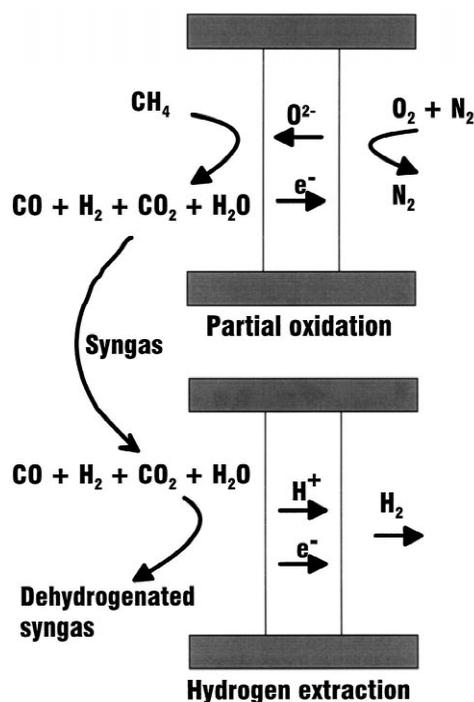


Fig. 1. Schematic use of mixed oxygen ion–electronic conductor for oxygen separation with direct partial oxidation of methane, followed by use of mixed protonic–electronic conductor for hydrogen extraction.

mixed protonic–electronic conduction. Focus will be on oxide and hydroxide systems, although other classes of materials can be of interest also.

Under the reducing conditions the materials will to a large extent comprise metal cations in lower oxidation states than we are used to. Furthermore, the interest in utilising proton conduction in oxides or hydroxides under reducing conditions has happened to coincide with recent indications in our laboratory of transport of hydride ions in oxides under such conditions [2,3]. The present opportunity will be used to introduce this new aspect of hydrogen ion transport and to point at some consequences hydride ions may have for the application of proton conducting membranes. However, we will first treat the, by now, more traditional theory of mixed proton transport, and make the comments about the hydride ions at the end.

## 2. Electrochemical gas permeation theory

In developing the necessary theory for hydrogen permeation in a mixed conductor, we start by assuming that the flux of each charge carrier species  $k$  is driven by chemical and electrical forces only, and that it is proportional to a transport coefficient, like the diffusivity, conductivity, or mobility, of that species (i.e. we neglect cross-terms in this treatment). If we choose to use the conductivity of the species, the flux is:

$$j_k = \frac{-\sigma_k}{z_k e^2} \left( \frac{d\mu_k}{dx} + z_k e \frac{d\phi}{dx} \right) \quad (1)$$

The terms in the parenthesis represent the chemical and electrical potential gradient, and  $z_k e$  is the charge of the species. We sum up all the partial electrical currents resulting from all fluxes and require that their sum, the net current, is zero in a membrane without any external electrical circuit:

$$I_{\text{total}} = \sum_i z_i e j_i = \sum_i \frac{-\sigma_i}{z_i e} \left( \frac{d\mu_i}{dx} + z_i e \frac{d\phi}{dx} \right) = 0 \quad (2)$$

The summation is over all species considered significant, typically oxygen ions, protons, and electrons. Eq. (2) can be solved with respect to the electrical potential gradient:

$$\frac{d\phi}{dx} = \sum_i \frac{-t_i}{z_i e} \frac{d\mu_i}{dx} \quad (3)$$

where  $t_i$  is the transport number of species  $i$  (integration of Eq. (3) would give the open-circuit voltage of a concentration cell). We insert Eq. (3) into Eq. (1) and obtain:

$$j_k = \frac{-\sigma_k}{z_k e^2} \left( \frac{d\mu_k}{dx} - z_k \sum_i \frac{t_i}{z_i} \frac{d\mu_i}{dx} \right) \quad (4)$$

Now, we introduce equilibria between neutral and charged species in the cases we want to include. For oxides and hydroxides, it may, for instance, be natural to consider transport by oxygen ions, protons, and electrons, so that we may use the following two equilibria:



$$d\mu_{\text{O}} + 2d\mu_{e^-} = d\mu_{\text{O}^{2-}} \quad (6)$$

and

$$\text{H} = \text{H}^+ + e^- \quad (7)$$

$$d\mu_{\text{H}} = d\mu_{\text{H}^+} + d\mu_{e^-} \quad (8)$$

We insert this into Eq. (4) for the desired species  $k$  and utilise that the sum of all transport numbers equals unity. Thus, for the flux of oxygen ions we get:

$$j_{\text{O}^{2-}} = \frac{-\sigma t_{\text{O}^{2-}}}{4e^2} \left[ (t_{e^-} + t_{\text{H}^+}) \frac{d\mu_{\text{O}}}{dx} + 2(t_{\text{H}^+}) \frac{d\mu_{\text{H}}}{dx} \right] \quad (9)$$

If we assume and insert  $d\mu_{\text{O}} = 1/2 d \ln p_{\text{O}_2}$  and  $d\mu_{\text{H}} = 1/2 d \ln p_{\text{H}_2}$  we further obtain:

$$j_{\text{O}^{2-}} = \frac{-kT\sigma t_{\text{O}^{2-}}}{8e^2} \left[ (t_{e^-} + t_{\text{H}^+}) \frac{d \ln p_{\text{O}_2}}{dx} + 2(t_{\text{H}^+}) \frac{d \ln p_{\text{H}_2}}{dx} \right] \quad (10)$$

which, upon integration over the membrane thickness gives:

$$j_{\text{O}^{2-}} = \left[ \frac{-kT}{8e^2} \int_{p_{\text{O}_2}^o}^{p_{\text{O}_2}^i} \sigma t_{\text{O}^{2-}} (t_{e^-} + t_{\text{H}^+}) d \ln p_{\text{O}_2} + \frac{-kT}{4e^2} \int_{p_{\text{H}_2}^o}^{p_{\text{H}_2}^i} \sigma t_{\text{O}^{2-}} t_{\text{H}^+} d \ln p_{\text{H}_2} \right] \frac{1}{X} \quad (11)$$

where  $X$  is the total thickness of the membrane, and the flux obtained is defined as going from conditions  $i$  to conditions  $o$  (e.g. inner to outer). It may be noted that the expression in the square brackets is of the form of a rate constant for a growing oxide scale.

In a similar manner, we obtain for the proton flux:

$$j_{\text{H}^+} = \frac{-kT\sigma t_{\text{H}^+}}{4e^2} \left[ t_{\text{O}^{2-}} \frac{d \ln p_{\text{O}_2}}{dx} + 2(t_{e^-} + t_{\text{O}^{2-}}) \frac{d \ln p_{\text{H}_2}}{dx} \right] \quad (12)$$

$$j_{\text{H}^+} = \left[ \frac{-kT}{4e^2} \int_{p_{\text{O}_2}^o}^{p_{\text{O}_2}^i} \sigma t_{\text{H}^+} t_{\text{O}^{2-}} d \ln p_{\text{O}_2} + \frac{-kT}{2e^2} \int_{p_{\text{H}_2}^o}^{p_{\text{H}_2}^i} \sigma t_{\text{H}^+} (t_{e^-} + t_{\text{O}^{2-}}) d \ln p_{\text{H}_2} \right] \frac{1}{X} \quad (13)$$

Combinations of the various transport numbers in the above will lead to transport of mainly oxygen or mainly hydrogen, and with a varying amount of water vapour transport in addition. Transport of water vapour is not of interest as such, but in limited amounts it need not be a problem. In hydrogen separation it may even be considered a useful way of avoiding too reducing conditions on the outlet side of the membrane (given that the inlet side contains some oxygen source, for instance,  $\text{CO}_2$  or water vapour).

In the following we will restrict ourselves to materials which are only protonic–electronic conductors, i.e. that have no oxygen ion transport. In this case, Eq. (13) simplifies to:

$$j_{\text{H}^+} = \left[ \frac{-kT}{2e^2} \int_{p_{\text{H}_2}^o}^{p_{\text{H}_2}^i} \sigma t_{\text{H}^+} t_{e^-} d \ln p_{\text{H}_2} \right] \frac{1}{X} \quad (14)$$

With this simple expression we may calculate the flux if we know how the conductivity and transport numbers vary with hydrogen activity so that we can perform the integration. Let us in the forthcoming cases consider oxides, and assume that electronic conduction dominates, so that the electronic transport number is unity. The protonic conductivity remaining in the integral is proportional to the concentration of protonic defects, and we will elaborate on three cases:

Case 1: Protons are minority defects. In this case the concentration and conductivity of protons are proportional to  $p_{\text{H}_2\text{O}}^{1/2}$ . This is often referred to as Sievert's law behaviour. The integration then yields:

$$j_{H^+} = \frac{-kT}{e^2} \sigma_{H^+}^{\text{ref}} \left[ (p_{H_2}^o)^{1/2} - (p_{H_2}^i)^{1/2} \right] \frac{1}{X} \quad (15)$$

where  $\sigma_{H^+}^{\text{ref}}$  is the proton conductivity at the reference hydrogen pressure (1 atm).

Case 2: Protons and electrons are the dominating defects, as a result of reduction by hydrogen. In this case we have  $\sigma_{H^+} \propto p_{H_2O}^{1/4}$ , and we obtain, after integration:

$$j_{H^+} = \frac{-2kT}{e^2} \sigma_{H^+}^{\text{ref}} \left[ (p_{H_2}^o)^{1/4} - (p_{H_2}^i)^{1/4} \right] \frac{1}{X} \quad (16)$$

Case 3: Proton defects are dominating and present at constant concentration, as a result of protons fully compensating acceptor dopants, or of an intrinsic proton content (e.g. acids or hydroxides). In this case  $\sigma_{H^+}$  is independent of  $p_{H_2O}$ , and integration yields:

$$j_{H^+} = \frac{-kT}{2e^2} \sigma_{H^+}^{\text{ref}} \left[ \ln p_{H_2}^o - \ln p_{H_2}^i \right] \frac{1}{X} \quad (17)$$

With these expressions we may calculate how fluxes vary as a function of the applied gradient in hydrogen partial pressure in the three cases. Fig. 2 shows the permeation of  $H_2$  gas (in  $\text{ml}_n H_2 \text{ min}^{-1} \text{ cm}^{-2}$ ) through a  $100 \mu\text{m}$  thick membrane at  $1000 \text{ K}$  assuming that the material has a rate limiting protonic conductivity of  $0.1 \text{ S cm}^{-1}$  at  $1 \text{ atm } H_2$ . The  $x$ -axis shows the hydrogen pressure at the high-pressure side, while the effective pressure on the low pressure side is assumed to be  $0.1 \text{ atm } H_2$ , typically representative of a pumped system. Fig. 3 shows a similar set of permeations, but here the working pressure on the low-pressure side is  $1 \text{ atm } H_2$ , i.e. a typical non-pumped situation. The permeation curves can be applied to different conductivity levels or

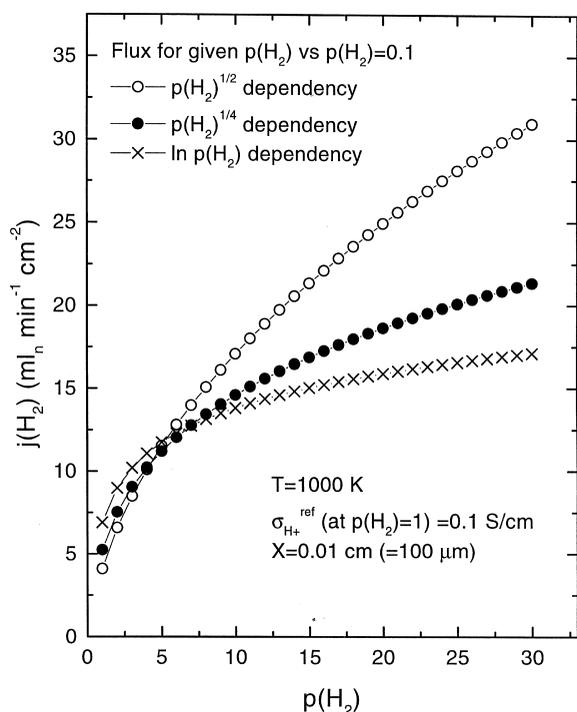


Fig. 2. Flux of hydrogen through a mixed conducting membrane with a given rate limiting proton conductivity, thickness, and defect model, as a function of the hydrogen pressure at the high pressure side, assuming a pressure of 0.1 at the low pressure side.

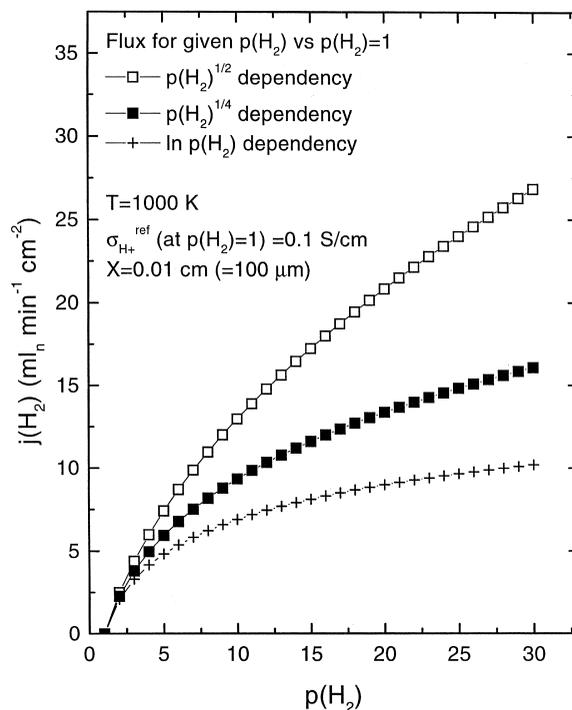


Fig. 3. Flux of hydrogen through a mixed conducting membrane with a given rate limiting proton conductivity, thickness, and defect model, as a function of the hydrogen pressure at the high pressure side, assuming a pressure of 1.0 at the low pressure side.

membrane thicknesses by simple parallel shifts, of course.

### 3. Literature cases

Experimental studies which can be compared with the above theory have been limited so far for proton conductors. Rare earth-doped BaCeO<sub>3</sub> is a mixed n-type electronic, oxygen ion and protonic conductor in H<sub>2</sub> + H<sub>2</sub>O atmospheres [4]. Balachandran et al. [5] investigated hydrogen flux through Y-doped BaCeO<sub>3</sub> exposed to N<sub>2</sub> + 4% H<sub>2</sub> vs. pure Ar at 600–800°C. They found that a second electronically conducting phase had to be added to get substantial permeation. A 0.20-mm thick composite membrane of this kind gave a flux of 0.12 ml<sub>n</sub> H<sub>2</sub>(g) min<sup>-1</sup> cm<sup>-2</sup> at 800°C. It is not possible to evaluate this in a way directly comparable to the theory presented or the data depicted in Fig. 2; more, and well defined, flux measurements on this important class of protonic conductors are surely in demand.

Nigara et al. [6] have done similar tests of hydrogen permeation through Ca-doped CeO<sub>2</sub> and undoped CeO<sub>2</sub> [7] at temperatures in the range 1000–1800 K. The permeabilities were similar in the doped and undoped ceria, and orders of magnitude lower than for the short-circuited BaCeO<sub>3</sub>. For the undoped CeO<sub>2</sub> they estimated the proton conductivity to be around 10<sup>-5</sup> S cm<sup>-1</sup> at 800°C, which is very minor compared to the high oxygen ion conductivity in these materials.

There is a great need to investigate more materials, and below we will mention a few classes of potential mixed proton–electron conductors. Before doing so, we note from the existing literature cases that detecting hydrogen permeation reliably at high temperatures represents a considerable challenge, for instance, in terms of high temperature sealing.

### 4. Classes of potential materials candidates

In order to be protonic conductors, candidate materials must contain a proton sublattice with defects or contain non-structural protonic interstitial defects. The protonic defect concentration may be

increased by doping or non-stoichiometry. The material must also be a good electronic conductor and thus contain mixed-valency elements. The smallest out of the protonic and electronic conductivities must usually be at least 0.1 S cm<sup>-1</sup>, depending on membrane thickness and other factors. Most important, perhaps, is that we are dealing with reducing conditions. We may have to consider unusually low oxidation states, and/or that n-type conduction will be relatively more important than the p-type conduction often encountered in, for instance, oxygen permeable membranes. Based on the above, the development of materials with mixed protonic–electronic conduction may follow different, often overlapping, strategies.

#### 4.1. Acceptor doping

Acceptor doping of oxides or other nominally proton-free compounds increases the concentration of protons, and also of electron holes, yielding p-type conduction. As the latter often vanishes under reducing conditions, one can use cations in low oxidation states such that they may be p-type conductors even under reducing conditions (see for instance Cr<sup>3+</sup> in LaCrO<sub>3</sub>). Alternatively, one has to utilise n-type conduction, which may be considerable in many cases under reducing conditions even in an acceptor-doped material. The latter is achievable with a reducible cation, as illustrated by the n-type conduction of acceptor-doped SrCeO<sub>3</sub> and BaCeO<sub>3</sub> under reducing conditions. An alternative is to dope with an aliovalent cation with ambivalent character, which may enhance the electronic conduction (n- or p-type). It is noteworthy, however, that acceptor-doping of oxides giving high protonic conductivity typically results also in a high concentration of oxygen vacancies.

#### 4.2. Proton incorporation by reduction with hydrogen

Proton incorporation by reduction with hydrogen takes place in oxides by the reaction H<sub>2</sub>(g) + 2O<sub>O</sub><sup>•</sup> = 2OH<sub>O</sub><sup>•</sup> + 2e' and creates protonic and electronic defects directly. A somewhat reducible cation is thus desirable. This kind of defect structure was first

demonstrated in ZnO [8], but a number of other binary oxides of reducible cations should be investigated with respect to hydrogen uptake at the respective temperatures where they are stable in hydrogen, e.g. TiO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub>. Also in this class of materials competition from oxygen vacancies (or metal interstitials) may be expected.

#### 4.3. *Metallic or intrinsically electronic compounds*

Metallic or intrinsically electronic compounds are of potential interest if the mixed valency giving rise to the half-filled bands or small band gaps exist and prevale under reducing conditions. However, proton concentration and mobility are in such materials most often unknown and need to be determined by methods different from conductivity studies, e.g. by chemical permeation measurements or isotope exchange/SIMS.

#### 4.4. *Intercalation compounds*

Many oxides take up large quantities of protons and/or hydrogen by intercalation, often at moderate temperatures. Examples include NiOOH, MnO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub> and WO<sub>3</sub> which may be reduced by hydrogen, forming hydroxides, oxyhydroxides and so-called bronzes. These may possess high concentrations and transport rates of protons or hydrogen at relatively low temperatures. However, many of them are not considered very stable in hydrogen at more elevated temperatures, as they (at least in the oxidised state) represent the cation in a valence typical of near-atmospheric oxygen pressures. Furthermore, it is difficult to find literature data on proton transport that can be directly translated into permeabilities, and a dedicated study aiming at producing such data would be very useful.

#### 4.5. *Materials with structural protons; hydroxides, oxyhydroxides, acids, hydrates*

The best low-temperature proton conductors contain structural protons, in which case it is necessary to promote proton transport by creating proton vacancies or interstitials by intrinsic (thermal) disorder or by doping. CsHSO<sub>4</sub>, with its thermally disordered protons in the high temperature phase,

provides an example. However, most of the established proton conductors in this class exhibit no electronic transport. Mixed conduction may, however, be foreseen in systems with mixed valency cations. For instance, the system NiOOH/Ni(OH)<sub>2</sub> is in operation in rechargeable electrodes in accumulators and expectedly transports both protons and electrons with relative ease. However, these hydroxides are not stable in hydrogen, and a check of thermodynamical properties of known hydroxides reveals that very few are stable in hydrogen over a useful range of temperature.

All in all, the number of potential candidates may not appear to be very large, but we may hope that the practical application and dedicated search itself may lead to discovery of new compounds with promising properties and which are stable under the conditions of interest.

### 5. **Presence, transport, and effects of hydride ions**

In the relatively short history of hydrogen defects in oxides, we have reached a common acceptance for the proton as the dominant defect; always bonded to an oxygen ion to form a hydroxide ion, but predominantly moving by the free proton mechanism, i.e. jumping between the oxygen hosts. Occasional reports of other hydrogen species in oxides have mainly been from spectroscopic studies at temperatures below ambient, e.g. for MgO [9] or based on rather ambiguous experimental indications at higher temperatures, e.g. for  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> [10]. Moreover, the transport of protons by hydroxide ion migration via oxygen vacancies can be but a minor contributor to conduction, and neither this nor hydroxide transport via interstitial sites has been found experimentally in solids.

A central method in identification of the charge carriers is the measurement of an electromotive force (emf) over a concentration cell. It has long been regarded as a standard technique for the determination of the ionic transport number for simple mixed conductors (e.g. using an oxygen activity gradient). However, the utilisation of combined gradients (e.g. in oxygen and hydrogen activities) to obtain transport numbers of native ions (oxygen and

metal ions) and hydrogen ions separately, is more complex, theoretically and experimentally, and has only been applied by a handful of groups. The central equation, fairly easily derived e.g. from Wagner type transport theory [11–14], expresses the open-circuit voltage over an oxide exposed to small gradients in oxygen and hydrogen activities. When expressed in terms of the partial pressures of oxygen and water vapour, the expression reads:

$$E_{II-I} = (t_{M+O} + t_{H^+} + t_{OH^-} - t_{H^-}) \frac{RT}{4F} \ln \frac{p_{O_2}^{II}}{p_{O_2}^I} - (t_{H^+} - t_{OH^-} - t_{H^-}) \frac{RT}{2F} \ln \frac{p_{H_2O}^{II}}{p_{H_2O}^I} \quad (18)$$

In this case we have chosen to include native ions (metal and oxygen), protons, hydroxide ions, and hydride ions (in addition to the implicitly included electrons). For a mixed proton, hydroxide ion, oxygen ion and electron conductor, the voltage measured with a gradient solely in  $p_{O_2}$  will give the total ionic transport number (including the two protonic defects), while with a gradient solely in  $p_{H_2O}$  (giving an equal gradient in  $p_{H_2}$ ) gives information of the transport numbers of the hydrogen-containing defects only. In particular, the sign of the voltage will be different for predominant transport of protons and hydroxide (or hydride) ions in a given gradient of  $p_{H_2O}$ . In the history of this particular type of measurement all results have been reported with a sign in accord with proton transport, and this has in our opinion been the clearest evidence for proton transport, and against hydroxide ion migration.

Nevertheless, a few years ago, we began noting that, for certain oxides, the voltage of water vapour concentration cells changed sign upon going to more reducing conditions.

The effect seemed to become more pronounced at higher temperatures. We were initially rather sceptical of the significance of these observations, and have hesitated to draw conclusions and publish. However, the number of observations has increased and the models matured, and they all point in the direction of substitutionally dissolved hydride ions,  $H^-$ , or, in defect notation:  $H_O^-$ .

Figs. 4 and 5 show data for partial conductivities of, respectively, undoped  $SrTiO_3$  and 1 mol%  $CaO$ -

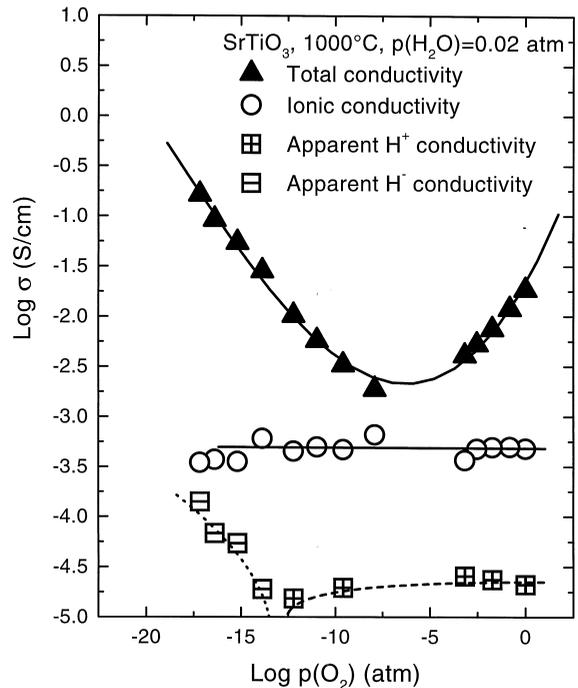


Fig. 4. Conductivities in nominally undoped  $SrTiO_3$  at 1000°C vs. oxygen partial pressure in wet atmospheres. The total conductivity is from two-point AC measurements, while the partial conductivities are obtained from emf measurements with gradients in  $p_{O_2}$  (ionic) or  $p_{H_2O}$  (protons and hydride ions). Data adapted from Refs. [2,3].

doped  $Nd_2O_3$ , measured and evaluated according to Eq. 18 above. The points marked as showing apparent hydride ion conductivity had emf values with opposite sign of those showing proton conductivity. The former must thus be assigned to a negative hydrogen species; hydride or hydroxide ions. Since the experiment measures the sum of contributions from the positive and negative hydrogen species, we can only say which is the higher. Furthermore, the shift is of such a nature that the emf necessarily goes through zero, and the deduced partial hydrogen ion conductivities thus appear to become zero at some point. This is indicated in the guide-for-the-eye lines in Figs. 4 and 5.

Neither the defect chemistry nor transport mechanisms of hydroxide ions allow their conductivity to increase with decreasing  $p_{O_2}$  at constant  $p_{H_2O}$  in such a way that it could overtake that of free proton transport (this reflects that the oxidation state of

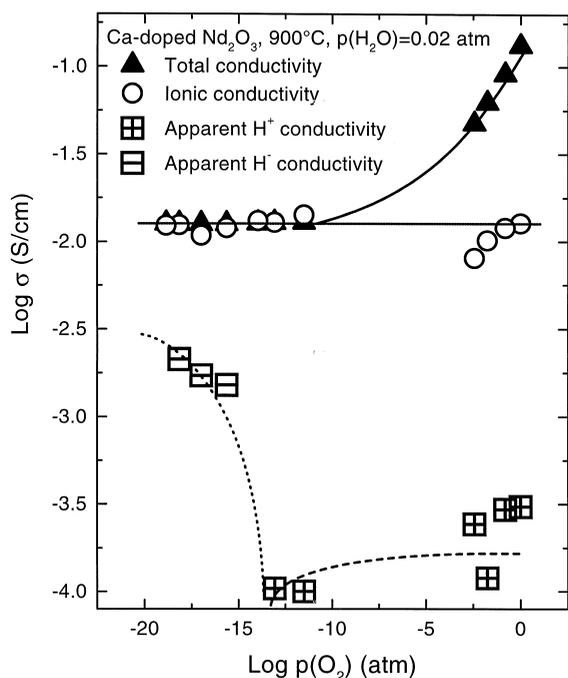
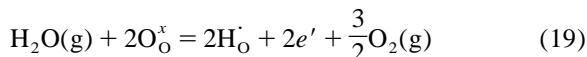


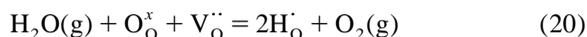
Fig. 5. Conductivities in 1 mol% CaO-doped  $\text{Nd}_2\text{O}_3$  at  $900^\circ\text{C}$  vs. oxygen partial pressure in wet atmospheres. The total conductivity is from two-point AC measurements, while the partial conductivities are obtained from emf measurements with gradients in  $p_{\text{O}_2}$  (ionic) or  $p_{\text{H}_2\text{O}}$  (protons and hydride ions) [18].

hydrogen is the same in the hydroxide, in the proton, and in water). However, the defect chemistry of hydride ions does predict such a change, as we will show. Since hydride ions are large and the structure (at least of the perovskite) is close-packed, we disregard the possibility of interstitial hydride ions, and concentrate on substitutional hydride ions.

The dissolution of substitutional hydride ions from water vapour can be written:



In order to visualise the behaviour under a defect situation dominated by oxygen vacancies, we may alternatively write:



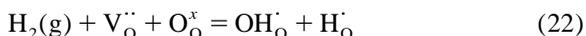
which tells us that the concentration of substitutional hydride ions,  $[\text{H}_\text{O}^\cdot]$ , will be proportional to  $p_{\text{O}_2}^{-1/2}$ ,

when  $p_{\text{H}_2\text{O}}$  is constant and the defect structure is dominated by a constant concentration of oxygen vacancies (e.g. compensating acceptor dopants).

It is also interesting to look at the equilibrium between protons (as hydroxide) and hydride ions:



As long as the concentration of protons is independent of  $p_{\text{O}_2}$  (as it is in our cases) this equilibrium again states that  $[\text{H}_\text{O}^\cdot]$  will be proportional to  $p_{\text{O}_2}^{-1/2}$ . Thus, the increase of hydride ion concentration with decreasing  $p_{\text{O}_2}$  does not imply that the proton concentration goes down; they exist side by side. Their co-existence can be seen as a disproportionation of the molecular hydrogen which is present in the gas phase under the reducing conditions in question:



At sufficiently low  $p_{\text{O}_2}$  (and high  $p_{\text{H}_2\text{O}}$ ) the concentration of hydride ions may surpass that of the oxygen vacancies, so that the limiting electroneutrality becomes  $[\text{H}_\text{O}^\cdot] = [\text{A}'] = \text{constant}$ , where  $\text{A}'$  is the acceptor dopant. At this point the new defect structure enforces new dependencies of many defects; for instance, the concentration of protons would start to decrease with decreasing  $p_{\text{O}_2}$ .

A number of interesting features will be related to the presence of hydride ions. We have so far looked at the sign of the emf of a water vapour concentration cell. However, also the sign of the oxygen concentration cell (or of a fuel cell for that matter) would change if the hydride ions became the dominating charge carriers (see Eq. (18)). However, with substitutional hydride ions, this situation cannot be realised: The conductivity of substitutional hydride ions can namely not surpass the conductivity of the oxygen vacancies; the transport of hydride ions via oxygen vacancies can only be upheld by an equal or higher supply of vacancies. Thus, the conductivity of hydride ions will not surpass a plateau somewhere below the oxygen vacancy conductivity. This is obeyed in the data in Figs. 4 and 5. However, the number of substitutional hydride ions may still increase, and they would eventually depress the

number of vacancies sufficiently that both conductivities go down with decreasing  $p_{O_2}$ .

While hydride ion conductivity by substitutional hydride ions moving via vacancies must be lower than oxygen vacancy conductivity itself, we also have the restriction on our measurements that the hydride ion conductivity can only be observed by our emf method if it is higher than the proton conductivity. Hydride ion conduction may thus only be visible in a relatively narrow window between proton conduction and a higher oxygen vacancy conduction. In a material where proton conduction dominates over oxygen vacancy conduction, hydride ion transport may not be observed by these means. This may explain why this phenomenon has remained undiscovered for the many prominent high temperature proton conductors, such as the alkali earth cerates and zirconates.

Assume a membrane in a gradient of  $p_{O_2}$ , e.g. a fuel cell or electrolyser. In our new defect chemical setting, one may have predominantly hydride ions at the reducing side and protons at the oxidising side. This may reduce the voltage of the fuel cell, and it may result in some strange phenomena in the electrolyser, like buildup of destructively high partial pressures of hydrogen inside the membrane.

On the other hand, new possibilities arise for hydrogen permeable membranes; in principle, hydrogen can permeate via ambipolar diffusion of protons and substitutional hydride ions (without electron transport) in a gradient of  $p_{H_2}$ . While this requires also local transport of oxygen via vacancies, a net oxygen transport may be stopped by appropriate control of the water vapour pressure gradient.

The hydride ions may be introduced as a species in the transport theory we used earlier to calculate hydrogen permeation, and we may in principle predict the effects of the hydride species. However, the correlation with oxygen vacancy transport and the transport of hydrogen by both positive and negative species will make the treatment rather complicated and outside the scope of this paper.

An interesting possibility lies in open structures (e.g. pyrochlores, rare earth oxides, or brownmillerites) where interstitial hydride ions can be imagined, and which are not dependent on oxygen vacancy supplies for migration.

## 6. Concluding remarks

We have briefly touched upon the simplest possible (Wagner type) theory for proton transport in mixed conducting membranes and seen theoretical examples of flux calculations. The few materials investigated in practice, mainly oxides with reducible cations, have shown modest qualities with respect to use as hydrogen separation membranes. Strategies for further search have been pointed out. However, one should bear in mind that a ceramic mixed conducting hydrogen separation membrane is but one of a number of possibilities for hydrogen separation, probably with its strength in high temperature applications, where one wants to utilise the heat contained in the in-stream.

We have furthermore pointed at indications of the presence and migration of hydride ions in oxides under reducing conditions, probably as substitutionally dissolved defects,  $H_O^-$ . We have furthermore briefly touched upon some effects, possibilities and complications that this defect may introduce. Upon facing this new species one realises that reports of the co-existence of hydride and oxygen ions in terms of defects are practically non-existent, and that only very few ionic oxyhydrides are known ( $LaHO$  [15],  $TiH_xO_y$  [16,17]). Similarly, the co-existence of hydride ions and protons is almost unheard of. Thus, the whole thing opens up as a wide, new field of interest. One needs not go further than the oxidation of metals (at high or low temperature) or the use of metal hydride batteries or storage to realise that this is a field of immense general importance: In these systems we know that we may have hydride ions or hydride phases in the metal, while right outside we have protons or hydroxide ions. Technologically, it is fortunate that some metals develop protective scales while others exchange hydrogen and electrons with the surroundings at very high rates. What goes on in the thin interface layers of oxides or hydroxides is often mainly unknown, and for us to discover.

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