Modeling and analysis of hydrogen permeation in mixed proton–electronic conductors

Lin Li\textsuperscript{a,b,1}, Enrique Iglesia\textsuperscript{a,b,*}

\textsuperscript{a}Department of Chemical Engineering, University of California at Berkeley, Berkeley, CA 94720-1462, USA
\textsuperscript{b}Division of Materials Sciences, E.O. Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

Received 22 August 2002; received in revised form 20 January 2003; accepted 27 January 2003

Abstract

A rigorous model for hydrogen permeation through dense mixed conductors was derived using the formalism of non-equilibrium thermodynamics for various operating modes and process conditions. The concentrations of charge carriers were rigorously included in this model through defect equilibria with the chemical environment at each membrane surface and through balance equations and a virtual pressure formalism within the membrane. Hydrogen permeation rates through proton–electron–hole mixed conductors were simulated using this framework under open-circuit, short-circuited, and applied potential operating modes. The sensitivity of H\textsubscript{2} permeation rates to the reduction–oxidation potentials at each side of the membrane and to the membrane properties (e.g. electron/hole diffusivity, oxygen binding energy) was examined in terms of the mobility and concentration of each charge carrier in order to identify rate-limiting steps for H\textsubscript{2} transport. These simulations showed that electronic transport controls H\textsubscript{2} permeation rates in proton–electron–hole mixed conductors typically used for H\textsubscript{2} permeation, especially when hydrogen chemical potentials are significantly different in the two sides of the membrane. These electronic conduction limitations arise from a region of very low electronic conductivity within the membrane, caused by a shift in the predominant charge carriers from electron to holes with decreasing hydrogen chemical potential. Under these asymmetrical conditions, H\textsubscript{2} permeation rates increase more markedly when an external electron-conducting path is introduced than at lower chemical potential gradients. Such interplay between rate-controlling variables leads to complex effects of H\textsubscript{2} chemical potential gradients on permeation rates. The effects of intrinsic membrane properties on H\textsubscript{2} permeation were examined by systematic changes in the defect equilibrium constants. A decrease in oxygen binding energy, manifested in a stronger tendency for reduction of the oxide membrane material, leads to higher electron concentrations and to higher rates for open-circuit operation, during which electron conduction limits H\textsubscript{2} transport rates.

© 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Model; Simulation; Mass transfer; Membrane; Proton conduction

1. Introduction

Metal oxides with mixed ionic–electronic (ambipolar) conductivity have attracted considerable attention as dense membranes useful in separations, chemical reactors, and fuel cells. Most studies of ionic transport through dense oxides have focused on oxygen-permeable materials (Bouwmeester & Burggraaf, 1996), but high-temperature proton conductors have been known for some time (Iwahara, 1996; Nowick & Du, 1996; Kreuer, 1997, 1999, 2000; Norby, 1999). The defect chemistry and the proton conductivity of these materials under electrochemical conditions has been studied, but few reports have addressed the ability of these materials to permeate hydrogen (Balachandran et al., 2001; Guan, Dorris, Balachandran, & Liu, 1998; Hamakawa, Hibino, & Iwahara, 2002; Li & Iglesia, 2001; Qi & Lin, 2000). As a result, kinetic and mechanistic descriptions of hydrogen permeation behavior through proton–electronic mixed conductors remain incomplete.

Some theoretical guidance is available from treatments of oxygen transport (Bouwmeester & Burggraaf, 1996), but the conditions and the relevant transport mechanisms differ significantly in these two systems. For example, both sides of oxygen transport membranes may be in contact with oxidizing streams. Under such conditions, the required electronic conduction is carried out by holes (p-type conduction). In
contrast, H₂ permeation involves at least one side exposed to a reducing environment. This leads to very low hole conductivities, because hole concentrations in acceptor-doped perovskites decrease with decreasing oxygen thermodynamic activity. These reducing or asymmetric (reducing in one side and oxidizing in the other) conditions lead to changes in rate-determining charge carriers as a function of position within the membrane thickness. The characterisation and prediction of the relevant rate processes require rigorous transport models of greater complexity than those needed for oxygen transport systems.

Recently, Norby and Larring (2000) reported a hydrogen permeation model for proton conductors. Their model describes the behavior of such systems for open-circuit conditions, in which no net current flows across the membrane and the electrical potential gradient equals the net chemical potential gradients for all charge carriers. Hydrogen flux equations were derived by assuming electron transference numbers of unity (conductivities much greater for electrons than for protons) and then expressing the flux as a function of the proton conductivity and the hydrogen partial pressure.

The dearth of permeation data remains a significant hurdle to the validation and improvement of available permeation models. Simulations based on the Norby and Larring (2000) model have not been compared with permeation data; also, this model is useful only for materials with high electronic conductivity, for which the hydrogen flux is controlled only by proton transport. Yet, H₂ permeation data indicate that electronic conduction is a kinetically relevant step in the overall transport process (Balachandran et al., 2001; Guan et al., 1998; Li & Iglesia, 2001; Qi & Lin, 2000). Proton conduction through dense membranes involves proton migration via hopping of hydrogen atoms among lattice oxygen atoms within the structure of perovskite materials, without concurrent motion of oxygen anions. Indeed, immobile oxygens, generally associated with electronic insulators, are essential in order to avoid oxygen migration and membrane over-reduction during hydrogen permeation (Bouwmeester & Burggraaf, 1996; Tuller, 1981; Smyth, 1992). Also, hydrogen separation membranes must be operated at relatively low temperatures (< 1000 K) in order to prevent oxygen permeation and membrane reduction. Electronic conductivities show higher activation energies than the corresponding conductivities for protons (Tuller, 1981; Smyth, 1992); as a result, electron transport rates are typically lower than proton transfer rates, leading to electron transference numbers significantly less than unity.

In all previous mass transfer models of mixed conductors (Norby & Larring, 2000; Guan et al., 1998; Qi & Lin, 2000), hydrogen permeation has been described in terms of proton and electronic conductivities that are taken either as constant across the membrane cross-section or as empirical functions of H₂ partial pressure. In reality, these conductivities, as defined, depend not only on the transport properties of the solid (i.e., charge carrier mobility), but also on the concentrations of each charge carrier. These concentrations, in turn, depend on the chemical composition of the contacting gas phase and on the position across the membrane thickness, because of the prevalent chemical potential gradients responsible for net mass transport. As a result, conductivities have retained a qualitative character in all previous attempts at rigorous descriptions of net transport rates, because they do not reflect merely the intrinsic properties of the materials, but depend also on conditions, the required details of which are not always reported or even measured in parallel experiments. Recently, Huggins (2001) discussed charge carrier transport inside solid electrolytes by using defect equilibrium diagrams, but his analysis focused on electrical properties of solid electrolyte material, and not on the rate of proton transfer processes.

We propose here a comprehensive model designed to describe hydrogen permeation behavior in proton–electron mixed conductor membranes. Such models, when accurate and rigorous, provide essential guidance in the design and understanding of mixed conducting materials. The model proposed uses the formalism of non-equilibrium thermodynamics in order to provide rigorous and accurate descriptions of transport processes as a function of chemical environment and operating modes. The identity of the limiting charge carriers is specifically probed with the objective of guiding the search for materials that overcome transport bottlenecks in currently available conductors.

2. Mass transfer model for proton–electron mixed conductor membranes

In mixed conductors, chemical and electrical potential gradients co-exist and they act as the driving force for mass transport. Along the dimension of net transport (x = membrane thickness), mass transfer rates per cross-sectional area (fluxes) for component k are given by (Bouwmeester & Burggraaf, 1996)

$$ J_k = -\frac{c_k D_k}{RT} \left( \frac{\partial \mu_k}{\partial x} - z_k F \frac{\partial \phi}{\partial x} \right). $$

In Eq. (1), the first and second terms represent transport driven by chemical and electrical potential gradients, respectively. If we choose component 1 as the basis component, the electrical potential gradient $d\phi/dx$ can be expressed as a function of the chemical potentials of all other charge carriers. The flux for species of 1 then becomes (Appendix I)

$$ J_1 = \frac{c_1 D_1}{A} \frac{I}{F} - \sum_{k=2}^{n} \frac{z_k^2 c_k D_k}{RT} \frac{d\mu_k}{dx} + \frac{c_1 D_1}{A} \sum_{k=2}^{n} \frac{z_k^2 c_k D_k}{RT} \frac{d\mu_k}{dx}, $$

where

$$ A = \sum_{k=1}^{n} z_k^2 c_k D_k. $$
Eq. (2) describes fluxes for each charge carrier as a function of both their chemical potential gradient and those for all other species. This gives rise to a significant practical hurdle, because it is difficult to measure the chemical potential of each charge carrier within the membrane material, as required for the solution of Eq. (2). Thus, we must describe these potentials as a function of the concentrations and chemical potentials of the gas-phase species (e.g., H₂, H₂O, O₂) in contact with each side of the membrane. If both sides are brought in contact with the same gas mixture, the concentrations of all charge carriers will ultimately reach equilibrium with this gas phase, and their concentrations and chemical potentials at each point will depend only on the thermodynamics of the gas–solid reactions responsible for these equilibria. In proton–electron–hole mixed conductors, charge carriers include protons (OH⁻), electrons (e⁻), electron holes (h⁺), and vacancies (V⁰).

For typical proton conductors, such as SrCe₀.₉₅Yb₀.₀₅O₃₋ₓ, the gas–solid reactions can be described by the following stoichiometric equations (Iwahara, 1996; Schober, Schilling, & Wenzel, 1996):

\[
\frac{1}{2}O_2 + V^0 \equiv O^\circ + 2h^+;
\]

(4)

\[
H_2 + 2O^\circ \equiv 2OH^- + 2e^-;
\]

(5)

\[
H_2O + V^0 \equiv O^\circ \equiv 2OH^-.
\]

(6)

These three reactions, however, are not independent, because the H₂, O₂, and H₂O partial pressures must satisfy the thermodynamics for the reaction:

\[
H_2 + \frac{1}{2}O_2 \equiv H_2O.
\]

(7)

At each point within the membrane material, the charge carrier concentrations can be considered to be in quasi-equilibrium with a set of virtual partial pressures of H₂, O₂, and H₂O (\(\pi_j\)). These virtual partial pressures act as surrogates for the chemical potentials of these respective species at each point within the solid (Boudart & Djega-Mariadassou, 1984). Therefore, the flux equations can be expressed as functions of gradients in the virtual pressures of hydrogen and water (Appendix A):

\[
j_{OH} = \frac{\varepsilon_{OH}}{\lambda} i - \frac{\varepsilon_{OH}}{2\lambda} \left[ (e_h\gamma_h + e_e\gamma_e) \frac{d\ln(\pi_{H^1})}{d\xi} \right] + 4\varepsilon_{eV}\gamma_{eV} \frac{d\ln(\pi_{e^-})}{d\xi},
\]

(8)

\[
j_{e^-} = \frac{2\varepsilon_{eV}\gamma_{eV}}{\lambda} i + \frac{\varepsilon_{eV} \gamma_{eV}}{\lambda} \left[ (e_h\gamma_h + e_e\gamma_e + e_{OH}) \frac{d\ln(\pi_{e^-})}{d\xi} \right] - (e_h\gamma_h + e_e\gamma_e) \frac{d\ln(\pi_{H^1})}{d\xi}.
\]

(9)

Eqs. (8) and (9) are general flux equations that describe mass transport in mixed conductor membranes. These flux equations can be simplified to obtain expressions for specific membrane compositions, chemical environments, and operating conditions, as we describe in detail below.

2.1. Open-circuit conditions

For open-circuit conditions (\(l = 0\)), the fluxes of protons and vacancies are given by

\[
(j_{OH})_{open} = -\frac{\varepsilon_{OH}}{2\lambda} \left[ (e_h\gamma_h + e_e\gamma_e) \frac{d\ln(\pi_{H^1})}{d\xi} \right] + 4\varepsilon_{eV}\gamma_{eV} \frac{d\ln(\pi_{e^-})}{d\xi},
\]

(10)

\[
(j_{e^-})_{open} = \frac{2\varepsilon_{eV}\gamma_{eV}}{\lambda} i + \frac{\varepsilon_{eV} \gamma_{eV}}{\lambda} \left[ (e_h\gamma_h + e_e\gamma_e + e_{OH}) \frac{d\ln(\pi_{e^-})}{d\xi} \right] - (e_h\gamma_h + e_e\gamma_e) \frac{d\ln(\pi_{H^1})}{d\xi}.
\]

(11)

At steady state, \(j_{OH}\) and \(j_{e^-}\) must be constant at every point within the membrane and the above equations can be re-arranged to give (Appendix A)

\[
\frac{d\ln(\pi_{H^1})}{d\xi} = \frac{4j_{e^-}}{e_h\gamma_h + e_e\gamma_e + e_{OH}} - \frac{2j_{OH}}{e_h\gamma_h + e_e\gamma_e + e_{OH}},
\]

(12)

\[
\frac{d\ln(\pi_{e^-})}{d\xi} = \frac{j_{e^-}}{e_h\gamma_h + e_e\gamma_e + e_{OH}} - \frac{2j_{OH}}{e_h\gamma_h + e_e\gamma_e + e_{OH}}.
\]

(13)

With appropriate boundary conditions, Eqs. (12) and (13) can be integrated to obtain \(j_{e^-}\) and \(j_{OH}\). The charge carrier concentrations involved in these two equations can be obtained from the interactions between gas-phase molecules and the membrane surface, as described in Section 3.

2.2. Short-circuited conditions

For short-circuited conditions, potential differences across the membrane become negligible because a connecting external conductor provides a path of negligible resistance for electron transport (i.e. \(d\Phi/dx = 0\)). Then, we obtain from Eq. (1)

\[
(J_{OH})_{closed} = -\frac{c_{OH}D_{OH}}{RT} \left( \frac{d\mu_{OH}}{dx} \right),
\]

(14)

\[
(J_{e^-})_{closed} = -\frac{c_{e^-}D_{e^-}}{RT} \left( \frac{d\mu_{e^-}}{dx} \right).
\]

(15)

By analogy with the open-circuit case, fluxes can be expressed as functions of the H₂ and H₂O virtual partial pressure gradients within the membrane and then re-arranged to give

\[
\frac{d\ln(\pi_{H^1})}{d\xi} = -\frac{2j_{OH}}{e_h\gamma_h + e_e\gamma_e + e_{OH}},
\]

(16)

\[
\frac{d\ln(\pi_{e^-})}{d\xi} = \frac{j_{e^-}}{e_h\gamma_h + e_e\gamma_e + e_{OH}} - \frac{2j_{OH}}{e_h\gamma_h + e_e\gamma_e + e_{OH}}.
\]

(17)

Eqs. (16) and (17) can then be integrated in order to obtain the fluxes, after applying appropriate boundary conditions.
and introducing a relation between charge carrier concentrations \( \dot{c}_V \) and \( \dot{c}_H \) and gas-phase concentrations \( \rho_{n_2}, \rho_w \).

### 2.3. Electrochemical pumping

The membrane system can also be operated as an electrochemical pump by applying a direct voltage across the two sides. In this case, Eqs. (8) and (9) are required in order to describe the flux. Comparing Eqs. (8) and (9) with Eqs. (10) and (11) and defining the transference numbers for protons \( t_{OH} \), vacancies \( t_V \), and electron/holes \( t_{el} \) as

\[
\begin{align*}
    t_{OH} &= \frac{c_{OH} D_{OH}}{A} = \frac{\dot{c}_{OH}}{\lambda}, \\
    t_V &= \frac{c_V D_V}{A} = \frac{\dot{c}_V}{\lambda}, \\
    t_{el} &= \frac{c_{el} D_{el} + c_{h} D_{h}}{A} = \frac{\dot{c}_{el} + \dot{c}_{h}}{\lambda},
\end{align*}
\]

the fluxes across the membrane become

\[
\begin{align*}
    j_{OH} &= t_{OH} i + (j_{OH})_{open}, \\
    j_V &= t_V i + (j_V)_{open},
\end{align*}
\]

In Eqs. (21) and (22), the first and second terms reflect mass transport driven by electrical potential gradients imposed by an external voltage and by chemical potential gradients imposed by different gas compositions in the two sides of the membrane, respectively. When proton transference numbers are independent of applied voltage, the flux depends linearly on the current \( i \) with a slope equal to \( t_{OH} \) and a \( \gamma \)-intercept given by the open-circuit hydrogen flux at a given chemical potential gradient across the membrane. In many cases, the proton transference number depends on the applied voltage, because membrane materials are semiconductors, and the relationship between the flux \( j_{OH} \) and the current density \( i \) becomes non-linear (Iwahara, 1999; Li & Iglesia, 2001).

![Fig. 1. Hydrogen flux under various operation modes. The solid and dashed lines represent the flux of membranes with \( t_{OH} = 1 \) and \( < 1 \), respectively.](image)

An external voltage can lead to higher proton fluxes. Eq. (21) shows that proton fluxes under electrochemical pumping conditions are linear functions of the current when \( t_{OH} \) is independent of applied voltage and the proton fluxes can become significantly greater than that under short-circuited conditions. A combination of hydrogen permeation rate measurements in these various operating modes can be used to determine the identity of the rate-controlling charge carriers and their respective electronic transference numbers. For example, comparisons of fluxes under open-circuit and short-circuited conditions give the average proton transference number \( t_{OH} \) (the slope of line AB in Fig. 1).

### 2.4. The relationship between fluxes of charge carriers \( J_{OH}, J_{V} \) and of molecules \( J_{H_2}, J_w \) and \( J_{O_2} \)

In general, the motion of vacancies and protons leads to transport of \( H_2, O_2 \) and \( H_2O \) across the membrane (the other two charge carriers, electrons and holes, do not directly contribute to the transport of molecular or atomic species). The specific origin of the proton cannot be rigorously established (from \( H_2 \) or \( H_2O \)) because of the \( H_2-H_2O \) equilibrium. Vacancies can react with either \( O_2 \) or \( H_2O \). However, the mass balance requires that

\[
\begin{align*}
    J_{OH} &= 2 J_{H_2} + 2 J_w, \\
    J_V &= -2 J_{O_2} - J_w.
\end{align*}
\]

The direction and magnitude of \( J_{H_2}, J_V \) and \( J_{O_2} \) depend on: (1) the chemical environment in each side of the membrane (e.g. \( H_2, H_2O \) and \( O_2 \) pressures); (2) the membrane properties (the thermodynamics for reactions (4)–(7)); and (3) the mobility of charge carriers \( (D_V, D_{OH}) \) within the membrane material.
For selective hydrogen permeation, the transport rates of vacancies must be much lower than that of protons. Then, \( J_V \approx 0 \) and \( J_w \approx 0 \), and
\[
J_{\text{H}_2} = 1/2 J_{\text{OH}}.
\]

3. Charge carrier concentrations in mixed conductors

For mixed conductors, the gas-phase composition influences charge carrier concentrations and their gradients across the thickness of the membrane material. In order to rigorously account for these changes as a function of gas-phase environment and location within the membrane, we must relate the concentration of each charge carrier to one another and to the external environment at each membrane surface. Simulations of hydrogen permeation using the approach described above require that we estimate charge carrier concentrations as a function of \( \text{H}_2 \text{O} \) and \( \text{H}_2 \) partial pressures.

For mixed conductors, these concentrations are obtained by considering the solid–gas reactions in Eqs. (4)–(7). In addition, electronic equilibrium requires that:
\[
0 \overset{\text{K}_{\text{e}}}{=} \text{h}^+ + \text{e}^-, \tag{26}
\]
and electrical neutrality imposes the additional constraint
\[
2c_{V} + c_{\text{OH}^+} + c_h = c_{\text{dopant}} + c_e, \tag{27}
\]
where \( c_{\text{dopant}} \) is the dopant concentration in the membrane. In \( \text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3-\gamma \) membrane, Yb acts as the dopant used in order to increase the electronic conduction of these materials.

The equilibrium between gas phase and membrane should be described using chemical potential, which poses a significant challenge. However, Kreuer (1999) proposed that interactions with gas-phase species can be described by assuming ideal behavior for all species involved in defect formation for cubic and distorted cubic perovskites. Therefore, we treated gas phase–membrane interaction as an ideal system, and we can then solve the concentrations of four charge carriers for a given set of \( \text{H}_2 \) and \( \text{H}_2 \text{O} \) partial pressure by combining the equilibrium of Eqs. (4)–(7) with the electrical neutrality condition (Eq. (26)) (Appendix B).

The charge carrier concentrations depend on the equilibrium constants for reactions (4)–(7) and (26) (\( K_1, K_2, K_w \) and \( K_e \)) for a given membrane composition (\( c_{\text{dopant}} = \) constant) and temperature; they can be expressed in this manner as functions of \( p_{\text{H}_2} \) and \( p_{\text{H}_2 \text{O}} \). Fig. 2 shows the concentrations of these four charge carriers with changes in \( p_{\text{H}_2} \) and \( p_{\text{H}_2 \text{O}} \) for \( \text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3-\gamma \) at 1000 K. The equilibrium constants, \( K_1, K_2, K_w \) and \( K_e \) reported by Schober, Friedrich, and Condon (1995) were used in these calculations. Water partial pressures influence proton concentrations more strongly than \( \text{H}_2 \) partial pressures, and the effect of the latter becomes more pronounced at high \( \text{H}_2 \) pressures (\( p_{\text{H}_2} > 100 \text{ Pa} \)). In contrast, \( p_{\text{H}_2} \) strongly influences electron and hole concentrations over the entire range of partial pressures. Electronic conduction is provided by electrons for reducing environments (high \( p_{\text{H}_2} \)) and by holes for less reducing conditions (low \( p_{\text{H}_2} \)). Therefore, the chemical composition of the gas streams influences not only the mass transfer driving force but also the charge carrier concentrations within the membrane, and hence the conductivities of charge carriers, as defined. Conductivities are also influenced by the equilibrium constants, the values of which depend on the membrane material. For example, a higher value of \( K_2 \) indicates a higher membrane affinity for hydrogen, while higher \( K_1 \) values reflect higher membrane affinities for oxygen. By
incorporating the dependence of charge carrier concentrations on $H_2$ and $H_2O$ partial pressures into the model equations derived in the previous section, hydrogen permeation rates can be predicted for mixed conducting membranes. The resulting simulations account rigorously for the effects of operating conditions on both the mass transfer driving force and the concentrations of charge carriers.

4. Simulation of hydrogen permeation behavior

For mixed conductors, the proton flux across the membrane is determined by the concentration and diffusivity of protons and by the electron transfer ability of the material, which is usually expressed as its electronic conductivity. As we will see later, the electronic conductivity is a function of position in the membrane because it depends on the electron concentration, which also varies with position. The effective electron-conducting ability of the membrane, which can be defined as an average electronic conductivity, depends on: (i) the concentrations of electrons and holes in the membrane and (ii) the diffusivities of electrons and holes. The concentrations of electrons and holes are determined by the properties of the materials (e.g., reducibility) and by the operating conditions. In this section, we examine the effects of membrane reducibility and diffusivity on proton fluxes.

Fig. 3 shows the effects of electron/hole diffusivity on proton flux under open-circuit and short-circuited conditions; the latter corresponds to very high electron/hole diffusivities (provided by the external circuit). For a given mass transfer driving force ($\ln(p_{H_2,1}/p_{H_2,2})$), the proton flux ($j_{OH}$) increases with increasing of electronic mobility, because charge neutrality requires the concurrent motion of protons and electron/holes. When $\gamma_e$ and $\gamma_h$ are very high ($>10^2$), additional increases in electronic mobility do not influence $H_2$ permeation rates, because fluxes become limited by proton mobility.

The relationship between the proton flux ($j_{OH}$) and the chemical potential driving force for mass transfer ($\ln(p_{H_2,1}/p_{H_2,2})$) depends on the electronic mobility of the membrane. In general, at low values of $\ln(p_{H_2,1}/p_{H_2,2})$ ($<5$), both sides of the membrane are exposed to reducing mixtures (symmetric operating mode) and electronic conduction occurs predominately via electron transport. Higher $\ln(p_{H_2,1}/p_{H_2,2})$ values will lead to higher proton transport rates, because average electronic transfer numbers will be largely independent of $\ln(p_{H_2,1}/p_{H_2,2})$. At sufficiently high $\ln(p_{H_2,1}/p_{H_2,2})$ values, however, the
high oxygen activity in the permeate side leads to very low electron concentrations and to low average electronic transference numbers. As a result, the higher mass transfer driving force imposed by these high electron concentration leads to a large increase in the electronic transfer number and to higher fluxes, because holes become the predominant charge carriers, at least in the membrane regions near the permeate side.

The effects of electron/hole diffusivity can also be examined by calculating electronic transference numbers (Eq. (20)) as a function of position within the membrane. Fig. 4 shows that $t_{el}$ depends strongly on position within the membrane for asymmetrical conditions \{ln($p_{H_2,1}/p_{H_2,2}$) = 45\}. At these conditions, the membrane regions near the process side interact with a highly reducing environment and electrons are the predominant electronic carriers. As $\xi$ increases, the virtual $H_2$ partial pressure decreases and the lower electron concentrations lead to lower electronic transference numbers. After reaching a minimum value, electronic transference numbers increase with increasing $\xi$ because the permeate side is exposed to oxidizing conditions, which lead to higher hole concentrations and more effective electronic conduction. This conclusion is consistent with electronic conductivity measurements reported by Hamakawa, Hibino, and Iwahara (1994). Under asymmetrical conditions, there is a transition region within which $t_{el}$ is very low and electron conduction determines the electronic conductivity and the hydrogen permeation rates. As the electron/hole mobility increases, the minimum $t_{el}$ increases and the low $t_{el}$ transition region becomes narrower; as a result, the average $t_{el}$ for the membrane increases.

Symmetrical conditions lead to reducing environments throughout the membrane thickness and the $t_{el}$ profile within the membrane is given by the left region in Fig. 4. Within this region, $t_{el}$ decreases with increasing $\xi$ because low $H_2$ virtual pressures lead to low concentrations of electrons; no increase in the electronic transference number is observed because the $H_2$ virtual pressure is never sufficiently low for holes to become the predominant charge carriers. The average $t_{el}$ is higher than under asymmetrical conditions and the effects of varying the electronic conductivity or of closing an external circuit on proton fluxes are stronger for asymmetrical (ln($p_{H_2,1}/p_{H_2,2}$) ~ 40) than for symmetrical (ln($p_{H_2,1}/p_{H_2,2}$) ~ 4) conditions.

Our simulations also show that the effects of the chemical nature of the permeate stream depend on the membrane reducibility and on the mobility of charge carriers. When electronic mobility is low, hydrogen permeation rates are controlled by electronic conductivity. In this case, a shift from reducing to oxidizing conditions in the permeate side (symmetrical to asymmetrical modes) leads to small effects in permeation rates. When the electronic conductivity is high, either because of the properties of the membrane properties or because of an external circuit, more oxidizing environments in the permeate side lead to larger permeation rates, because the corresponding increase in permeation driving force is not offset by a concurrent decrease in electronic conductivity as a result of changes in the permeate stream.

The reducibility of the membrane material (given by $K_1$ in our model) also influences hydrogen permeation rates. Higher values of $K_1$ reflect stronger oxygen binding and less reducible membrane materials. Fig. 5 illustrates the effect of varying $K_1$ on the electronic transference number $t_{el}$. As $K_1$ increases, electronic transference numbers within the more...
reducing regions of the membrane (near the process side) decrease because of a decrease in electron concentrations. The location of the minimum electronic transference number moves towards the process side, suggesting that the region within which electrons are the dominant charge carriers becomes thinner. For the range of $K_1$ values we examined, the average $t_{el}$ within the membrane decreases with decreasing of membrane reducibility. However, further increase of $K_1$ may lead to higher average $t_{el}$, because holes ultimately become the predominant charge carriers within a large fraction of the membrane thickness.

These findings suggest that for typical mixed conductors, such as SrCe$_{0.95}$Yb$_{0.05}$O$_3$, hydrogen permeation rates are largely controlled by electron conduction. Higher electronic conductivities will require higher concentrations or diffusivities of electrons or holes. In oxygen transport membranes, holes are the predominant charge carriers throughout the membrane thickness. In H$_2$ transport processes, at least one membrane surface is in contact with a strongly reducing environment; therefore, hole conduction cannot predominate throughout the entire membrane thickness. One potential solution is to increase electron concentration by selecting more reducible membrane materials. Reduction of membrane materials during operation, however, can lead to changes in the perovskite structure and to loss of mechanical integrity; thus, any such improvements in proton transport by increasing membrane reducibility is likely to be limited by these practical considerations.

In addition to its effects on electron/hole concentrations and $t_{el}$, the reducibility of the membrane also influences proton concentrations and hydrogen permeation rates. Figs. 6 and 7 show the effect of $K_1$ on proton flux under short-circuited and open-circuit operating modes, respectively. Under short-circuited conditions, $j_{OH}$ increases with increasing of $K_1$, and the sensitivity $j_{OH}$ to the driving force term $\ln(p_{H_2,1}/p_{H_2,2})$ increases, indicating that a given mass transfer driving force becomes more effective for H$_2$ transport as $K_1$ increases, because of the higher prevalent proton concentrations. In open-circuit mode, hydrogen permeation rates are largely controlled by electronic conduction. Therefore, higher values of $K_1$ lead to lower proton fluxes, as a result of the lower average electron concentrations prevalent as the membrane material becomes more difficult to reduce.

5. Usefulness and limitations of hydrogen transport model

The rigorous model presented here describes the transport properties of mixed conductors using the diffusivities and concentrations of each charge carrier as the fundamental relevant parameters responsible for net macroscopic motion. In doing so, it avoids the use of lumped phenomenological parameters, such as conductivities, which are appropriate for ideal electrical conductors, but not for the transport of chemical species through mixed conductors. The approach presented here also includes rigorous equilibria between the chemical environments in the process and permeate side and the defect species present at each membrane surface. As a result, the simulations implicitly contain the effects of these chemical environments on both the driving force for mass transfer and the concentrations of charge carriers.

One remaining issue, not currently treated in this model, is the potential effect of the chemical environment in the process and permeate side on the intrinsic mobility (diffusivity) of each charge carrier. Such effects may be important and difficult to measure, and they cannot be ruled out. We suggest, based on heuristic arguments and previous data, that they are not critical in determining transport rates. First, the concentrations of defects are small within typical membrane materials; therefore, non-idealities...
arising from defect–defect interactions are unlikely to arise. Also, Yajima and Iwahara (1992a, b) have found that measured proton mobilities do not depend on proton concentrations for SrCe0.95Yb0.05O3−δ. When required, such effects must be described in terms of the atomic-level bond-breaking and bond-breaking mechanisms responsible for migration of hydrogen and oxygen species within such solids. Recent examples show the emerging feasibility of such fundamental approaches for all charge carriers in mixed conductors (Kreuer, 1996, 1997, 1999, 2000), but detailed knowledge of charge carrier transport within these solids remains very limited.

External boundary layer or surface adsorption resistances can easily be incorporated into the hydrogen permeation model described here. Both of these effects are occasionally important for oxygen transport membranes (Bouwmeester & Burggraaf, 1996). Boundary layer effects have been neglected here for H2 transport membranes because H2 molecules diffuse much more rapidly than O2 molecules through a gas-phase boundary layer, while membrane permeation rates in practical applications are generally similar for both molecules. Dissociative chemisorption of H2 is expected to occur more rapidly than for O2, because of the smaller bond energies in H2. Also, H2 transport membranes must be operated below 1000 K in order to avoid oxygen transport and membrane over-reduction; as a result proton fluxes tend to be lower than for O2 transport membranes, which operate at much higher temperatures (~ 1300 K). Finally, our recent studies have shown that even for very thin SrCe0.95Yb0.05O3−δ (< 10 μm) films, the proton flux remains proportional to the inverse of the film thickness (Hamakawa, Li, Li, & Iglesia, 2002); thus, surface processes remain kinetically irrelevant even for very high H2 permeation rates. In some sense, this reflects the lower permeation rates for H2 in proton–electronic conductors at their typical temperatures (1 bar H2, 950 K; 5−3 S cm−1 for SrCe0.95Yb0.05O3−δ; Iwahara, 1996) than for O2 in oxide-electronic conductors (0.2 bar O2, 1273 K, 0.5 S cm−1; Bouwmeester & Burggraaf, 1996). Thus, it appears that the inclusion of external transport and adsorption kinetics is not required for currently available proton mixed conductor membranes. As H2 permeation rates continue to increase with advances in the hydrogen permeability of these materials, both external transport and H2 chemisorption kinetics must be rigorously described in order to replace the equilibrium between the surface and the bulk fluid assumed within the current model.

6. Conclusions

A mass transfer model for hydrogen permeation through proton–electronic mixed conductors was developed by using the formalism of non-equilibrium thermodynamics and describing the concentrations of all charge carriers through equilibrium with the contacting gas phase at surfaces and through a virtual pressure formalism within the membrane material. This model was used to describe H2 permeation through dense SrCe0.95Yb0.05O3−δ membranes. These simulations confirmed the rate-controlling role of electronic transport in H2 permeation processes, especially when the membrane is operated at very different hydrogen chemical potentials in the process and the permeate sides. Under such asymmetric operating conditions, an internal region with very low electronic transference number arises from a transition from electronic to hole conduction as the hydrogen chemical potential within the membrane decreases from high values near the process side to much lower values near the permeate side. As a result, when electronic mobility is high, either because of the nature of the membrane material or because of the presence of an external conducting circuit, large H2 chemical potential gradients across the membrane exploit the full driving force without the adverse effects of the lower electronic transport rates associated with such chemical potential gradients. When electronic transport limits H2 permeation rates, the full effects of these large chemical potential gradients cannot be exploited, because of their negative effects on electron transport rates. Improvements in electronic (and H2) transport rates require higher electron/hole diffusivities or more reducible membrane materials, which increase electron concentrations for a given chemical environment. Simulation results illustrate the nature and the underlying mechanism for the observed effects of the chemical environment in each side of the membrane on H2 permeation rates and how such effects depend on membrane properties, such as reducibility and charge carrier mobility. Heuristic arguments and experimental results are used to neglect the effects of external mass transport and of H2 dissociation rates on the rate of H2 permeation through typical mixed proton–electronic conductors. These external transport and adsorption effects can be readily incorporated into the current framework when the experimental situation requires it.

Notation

- $c_h$: concentration of charge carrier $k$, mol m$^{-3}$
- $C_T$: molar concentration of membrane (given by membrane density divided by molecular weight), mol m$^{-3}$
- $D_k$: diffusivity of charge carrier $k$, m$^2$s$^{-1}$
- $F$: Faraday constant C mol$^{-1}$
- $i$: Dimensionless current density
- $I$: total current density, A m$^{-2}$
- $I_k$: current density carried by charge $k$, A m$^{-2}$
- $j_k$: dimensionless flux of component $k$, defined by Eqs. (A.19) and (A.20)
- $J_k$: flux of component $k$, mol m$^{-2}$s$^{-1}$
- $K_e$: equilibrium constant, defined by Eqs. (B.1)-(B.4)
- $L$: membrane thickness, m
- $p_k$: partial pressure of component $k$, Pa
transference number of charge carrier \( k \)

\( t_k \)

distance along membrane thickness, m

\( x \)

charge on species \( k \)

\( z_k \)

Greek letters

\( \gamma_k \) dimensionless mobility of charge carrier \( k \), defined by Eqs. (A.22)–(A.24)

\( \nu_k \) dimensionless concentration of charge carrier \( k \), defined by Eqs. (A.25)–(A.28)

\( \eta_k \) electrochemical potential of species \( k \), J mol\(^{-1}\)

\( \lambda \) defined by Eq. (A.30)

\( \Lambda \) defined by Eq. (3)

\( \mu_k \) chemical potential of species \( k \), J mol\(^{-1}\)

\( \xi \) dimensionless distance, \( \xi = x/L \)

\( \pi_k \) virtual partial pressure of component \( k \), Pa

\( \phi \) electrical potential, V

Subscripts

\( h \) holes

\( e \) electrons

OH proton defect

\( V \) vacancy

\( w \) water

Acknowledgements

This work was supported by the Division of Fossil Energy of the U.S. Department of Energy (Contract No. DE-AC03-76SF00098) under the technical supervision of Dr. Daniel Driscoll.

Appendix A. Derivation of flux equations under various conditions

In mixed conductors, both chemical and electrical potential gradients can exist and act as the driving force for mass transport. In one dimension (\( x \)= membrane thickness dimension), the mass transfer rate per cross-sectional area (flux) of component \( k \) is given by (Bouwmeester & Burggraaf, 1996)

\[
J_k = - \frac{c_k D_k}{RT} \frac{d\eta_k}{dx},
\]

where \( \eta_k \), the electrochemical potential of component \( k \), contains both the chemical (\( \mu_k \)) and the electrical potentials (\( \phi \)) driving the transport of molecules across the membrane:

\[
\eta_k = \mu_k + z_k F \phi.
\]

Substituting Eq. (A.2) into Eq. (A.1), we obtain Eq. (1).

The charge current carried by component \( k \) is

\[
I_k = z_k F J_k,
\]

and the total current across the membrane is given by

\[
I = \sum_{k=1}^{n} I_k = I_1 + \sum_{k=2}^{n} z_k F J_k.
\]

Substituting the expression for \( J_k \) into Eq. (1), we obtain

\[
\sum_{k=2}^{n} z_k J_k = - \sum_{k=2}^{n} \frac{c_k D_k z_k^2}{RT} \frac{d\mu_k}{dx} - \sum_{k=2}^{n} \frac{c_k D_k z_k^2}{RT} F \frac{d\phi}{dx},
\]

and rearranging provides an expression for the electrical potential gradient:

\[
F \frac{d\phi}{dx} = \sum_{k=2}^{n} z_k J_k + \sum_{k=2}^{n} \frac{c_k D_k z_k^2}{RT} \frac{d\mu_k}{dx} - \sum_{k=2}^{n} \frac{c_k D_k z_k^2}{RT} F \frac{d\phi}{dx}.
\]

Substituting Eqs. (A.3), (A.4), and (A.6) into Eq. (1) we obtain Eq. (2).

From Eqs. (4)–(7),

\[
\mu_{H_2} = 2\mu_{OH} + 2\mu_e,
\]

\[
1/2\mu_{O_2} + \mu_{V} = 2\mu_{h},
\]

\[
\mu_{w} + \mu_{V} = 2\mu_{OH},
\]

\[
\mu_{H_2} + 1/2\mu_{O_2} = \mu_w.
\]

Based on Eqs. (A.7)–(A.10), the flux equations can be expressed as functions of gradients of chemical potential of hydrogen and water:

\[
J_{OH} = \frac{c_{OH} D_{OH}}{A} \frac{I}{F} - \frac{c_{OH} D_{OH}}{ART} \times \left[ \left( c_h D_h + c_e D_e \right) \frac{1}{2} \frac{d\mu_{H_2}}{dx} + 2c_{V} D_{V} \frac{d\mu_w}{dx} \right], \tag{A.11}
\]

\[
J_{V} = \frac{2c_{V} D_{V}}{A} \frac{I}{F} + \frac{c_{V} D_{V}}{ART} \left[ \left( c_h D_h + c_e D_e + c_{OH} D_{OH} \right) \frac{d\mu_w}{dx} - \left( c_h D_h + c_e D_e \right) \frac{d\mu_{H_2}}{dx} \right]. \tag{A.12}
\]

The chemical potential of \( H_2 \) and \( H_2O \) can be calculated in terms of their respective virtual pressures:

\[
\mu_{H_2}(\phi) = \mu^0_{H_2} + RT \ln(\pi_{H_2}), \tag{A.13}
\]

\[
\mu_{w}(\phi) = \mu^0_{w} + RT \ln(\pi_{w}), \tag{A.14}
\]

\[
\frac{d\mu_{H_2}}{dx} = RT \frac{1}{\pi_{H_2}} \frac{d\pi_{H_2}}{dx}, \tag{A.15}
\]

\[
\frac{d\mu_{w}}{dx} = RT \frac{1}{\pi_{w}} \frac{d\pi_{w}}{dx}. \tag{A.16}
\]
Then the flux equations can be expressed as functions of hydrogen and water partial pressure gradients:

\[ J_{\text{OH}} = \frac{c_{\text{OH}} D_{\text{OH}}}{\Lambda} \frac{I}{F} - \frac{c_{\text{OH}} D_{\text{OH}}}{2 \Lambda} \left( (c_{h} D_{h} + c_{e} D_{e}) \right) \times \frac{1}{\partial H_{2}} \frac{d \partial H_{2}}{d x} + 4 c_{v} D_{v} \frac{1}{\partial H_{2}} \frac{d \partial H_{2}}{d x}, \quad \text{(A.17)} \]

\[ J_{V} = \frac{2 c_{v} D_{v}}{\Lambda} \frac{I}{F} + \frac{c_{v} D_{v}}{\Lambda} \left( (c_{h} D_{h} + c_{v} D_{e} + c_{\text{OH}} D_{\text{OH}}) \frac{1}{\partial H_{2}} \frac{d \partial H_{2}}{d x} \right), \quad \text{(A.18)} \]

Eqs. (A.17) and (A.18) can be nondimensionalized to Eqs. (8) and (9) by defining

\[ j_{H} = \frac{J_{\text{OH}} L}{C_{T} D_{\text{OH}}}, \quad \text{(A.19)} \]
\[ j_{V} = \frac{J_{V} L}{C_{T} D_{\text{OH}}}, \quad \text{(A.20)} \]
\[ i = \frac{IL}{C_{T} D_{\text{OH}} F}, \quad \text{(A.21)} \]
\[ \gamma_{h} = D_{h}/D_{\text{OH}}, \quad \text{(A.22)} \]
\[ \gamma_{e} = D_{e}/D_{\text{OH}}, \quad \text{(A.23)} \]
\[ \gamma_{V} = D_{V}/D_{\text{OH}}, \quad \text{(A.24)} \]
\[ \delta_{h} = c_{h}/C_{T}, \quad \text{(A.25)} \]
\[ \delta_{e} = c_{e}/C_{T}, \quad \text{(A.26)} \]
\[ \delta_{V} = c_{V}/C_{T}, \quad \text{(A.27)} \]
\[ \delta_{\text{OH}} = c_{\text{OH}}/C_{T}, \quad \text{(A.28)} \]
\[ \zeta = x/L, \quad \text{(A.29)} \]
\[ \lambda = (C_{T} D_{\text{OH}}) = \delta_{h} \gamma_{h} + \delta_{e} \gamma_{e} + \delta_{\text{OH}} + 4 \delta_{V} \gamma_{V}, \quad \text{(A.30)} \]

where L the membrane thickness and CT is the molar concentration of the membrane.

For short-circuited conditions, using Eqs. (A.13)–(A.16), Eqs. (14) and (15) can be expressed as

\[ (J_{\text{OH}})_{\text{closed}} = -\frac{c_{\text{OH}} D_{\text{OH}}}{2 \partial H_{2}} \frac{d \partial H_{2}}{d x}, \quad \text{(A.31)} \]

\[ (J_{V})_{\text{closed}} = \frac{c_{V} D_{V}}{\partial H_{2}} \frac{d \partial H_{2}}{d x} - \frac{c_{V} D_{V}}{\partial H_{2}} \frac{d \partial H_{2}}{d x}, \quad \text{(A.32)} \]

The above equations can be non-dimensionlized as

\[ (j_{\text{OH}})_{\text{closed}} = \frac{c_{\text{OH}}}{2} \frac{d \ln(\partial H_{2})}{d \zeta}, \quad \text{(A.33)} \]

\[ (j_{V})_{\text{closed}} = \gamma_{V} \frac{d \ln(\partial H_{2})}{d \zeta}, \quad \text{(A.34)} \]

Eqs. (A.33) and (A.34) can be rearranged to give Eqs. (16) and (17).

**Appendix B. Calculation of charge carrier concentrations**

The corresponding equilibrium expressions for reactions \((4)–(7)\) and \((26)\) are given by

\[ K_{1} = c_{h}^{2} / c_{V} P_{O_{2}}^{1/2}, \quad \text{(B.1)} \]
\[ K_{2} = c_{OH}^{2} / c_{V} P_{H_{2}}, \quad \text{(B.2)} \]
\[ K_{w} = P_{w} / P_{H_{2}} P_{O_{2}}^{1/2}, \quad \text{(B.3)} \]
\[ K_{e} = c_{A} c_{e}. \quad \text{(B.4)} \]

Based on Eqs. (B.1)–(B.4), a non-linear equation is obtained for the proton concentration within the membrane:

\[ c_{\text{OH}}^{3} + ac_{\text{OH}}^{2} + bc_{\text{OH}} + c = 0, \quad \text{(B.5)} \]

where

\[ a = \frac{K_{1} K_{2} P_{H_{2}} P_{O_{2}}^{1/2}}{2 K_{e}^{2}} + \frac{K_{1} P_{O_{2}}^{1/2} \sqrt{K_{2} P_{H_{2}}}}{2 K_{e}}, \quad \text{(B.6)} \]
\[ b = -c_{\text{dopant}} \frac{K_{1} K_{2} P_{H_{2}} P_{O_{2}}^{1/2}}{2 K_{e}^{2}}, \quad \text{(B.7)} \]
\[ c = -\frac{K_{1} P_{O_{2}}^{1/2} (K_{2} P_{H_{2}})^{3/2}}{2 K_{e}}. \quad \text{(B.8)} \]

Then,

\[ c_{e} = \frac{\sqrt{K_{2} P_{H_{2}}}}{c_{\text{OH}}}, \quad \text{(B.9)} \]
\[ c_{h} = \frac{K_{e} c_{\text{OH}}}{\sqrt{K_{2} P_{H_{2}}}}, \quad \text{(B.10)} \]
\[ c_{V} = \frac{K_{2} c_{\text{OH}}^{2}}{K_{2} P_{H_{2}} K_{1} P_{O_{2}}^{1/2}}. \quad \text{(B.11)} \]

**References**


Schober, T., Friedrich, J., & Condon, J. B. (1995). Effective hydrogen diffusivity in SrCe$_{0.95}$Yb$_{0.05}$O$_{3-\delta}$ and SrZr$_{0.95}$Yb$_{0.05}$O$_{3-\delta}$. *Solid State Ionics, 75*, 175–179.


