



# Transport through mixed proton, oxygen ion and electron (hole) conductors: Goldman–Hodgkin–Katz-type equation

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## ARTICLE INFO

### Article history:

Received 7 April 2009

Received in revised form 22 May 2009

Accepted 3 June 2009

Available online 11 June 2009

### Keywords:

Proton

Oxygen ion

Fuel cell

Coupled transport

Onsager equations

## ABSTRACT

Many high temperature oxides and low temperature polymeric materials transport protons, oxygen ions, and electrons or holes. These materials are candidates as membranes for fuel cells and electrolyzers. This manuscript examines non-equilibrium steady state transport through such membranes under the assumption of local equilibrium. A simple equivalent circuit analysis is given for transport through mixed proton, oxygen ion, and electron (hole) conducting membranes. The cell potential can be described in terms of transport parameters of charged species ( $H^+$ ,  $O^{2-}$  and  $e$  or  $h$ ) and internal EMFs given in terms of chemical potentials of neutral species ( $\mu_{H_2}$ ,  $\mu_{O_2}$ ). The resulting equation for cell potential is similar to the Goldman–Hodgkin–Katz (GHK) equation used in cell physiology. Transport through a fuel cell based on such materials is examined. Effects of electrolyte/electrode interfaces are explicitly included in the analysis. Fluxes of  $H_2$  and  $O_2$  through the membrane are evaluated at open circuit and under load. They obey Onsager reciprocity relations, inclusive of interface effects. The analysis also shows that the chemical potentials of  $H_2$  and  $O_2$  and electric potential,  $\phi$ , exhibit abrupt changes across interfaces.

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## 1. Introduction

In aqueous systems of interest in cell physiology and other areas, transport of electrically charged species is commonplace. Examples include transport of ionic species across biological or polymeric membranes. In such cases, either side of the membrane has aqueous media containing ionic species in solution. Concentrations of the various ionic species are generally different on the two sides of the cell membrane. The cell membrane also typically contains water (hydrated). Transport of ionic species across cell membranes occurs under electrochemical potential gradients. Electrically charged species are ionic (cations and anions) and no net electrical current transports through the membrane. Several ionic species can be in solution and their transport occurs to varying degrees, depending upon their relative concentrations and mobilities. In a non-equilibrium steady state with concentrations of the various species in the two reservoirs assumed fixed, steady state fluxes of ionic species are established across the membrane. This leads to the establishment of an electrical voltage difference across the cell membrane, the cell potential, which can be described in terms of the concentrations of ionic species in the two reservoirs and their transport parameters across the membrane. The resulting equation is known as the Goldman–Hodgkin–Katz (GHK) equation

or sometimes as Goldman equation [1,2]. The GHK equation assumes equilibration of compositions of the various ionic species at liquid/membrane interfaces.

Aqueous and other liquid electrolyte solutions always contain mobile cations and mobile anions. Thus, local equilibrium can be described in terms of local chemical or electrochemical potentials of the ions. For example, for an ionic salt of the type  $M_mX_n$  dissolved in water, the dissociation reaction at equilibrium is



where the valence of the cation is  $n$  and that of the anion is  $-m$ . The corresponding local equilibrium may be given by

$$\mu_{M_mX_n} = m\mu_{M^{n+}} + n\mu_{X^{m-}} = m\tilde{\mu}_{M^{n+}} + n\tilde{\mu}_{X^{m-}} \quad (2)$$

where the  $\mu_i$ s are the respective chemical potentials and  $\tilde{\mu}_i$ s are the electrochemical potentials, the latter given by

$$\tilde{\mu}_i = \mu_i + z_i F \Phi \quad (3)$$

where  $z_i$  is the valence,  $F$  is the Faraday constant,<sup>1</sup> and  $\Phi$  is the local electrostatic potential. Although not commonly used, it is understood that local equilibria may additionally be given with respect to the neutral species by reactions of the type



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<sup>1</sup> All chemical potentials and electrochemical potentials are defined on a molar basis.

## Nomenclature

### List of symbols

$\ell$	electrolyte thickness (cm)
$r_e^c = \frac{\delta_c}{\sigma_e^c}$	cathode/electrolyte interface electronic area specific resistance ( $\Omega \text{ cm}^2$ )
$r_e^a = \frac{\delta_a}{\sigma_e^a}$	anode/electrolyte interface electronic area specific resistance ( $\Omega \text{ cm}^2$ )
$r_e^{\text{el}} = \frac{\ell}{\sigma_e^{\text{el}}}$	electrolyte electronic area specific resistance ( $\Omega \text{ cm}^2$ )
$r_{\text{O}_2^-}^c = \frac{\delta_c}{\sigma_{\text{O}_2^-}^c}$	cathode/electrolyte interface oxygen ion area specific resistance ( $\Omega \text{ cm}^2$ )
$r_{\text{O}_2^-}^a = \frac{\delta_a}{\sigma_{\text{O}_2^-}^a}$	anode/electrolyte interface oxygen ion area specific resistance ( $\Omega \text{ cm}^2$ )
$r_{\text{O}_2^-}^{\text{el}} = \frac{\ell}{\sigma_{\text{O}_2^-}^{\text{el}}}$	electrolyte oxygen ion area specific resistance ( $\Omega \text{ cm}^2$ )
$r_{\text{H}^+}^c = \frac{\delta_c}{\sigma_{\text{H}^+}^c}$	cathode/electrolyte interface proton area specific resistance ( $\Omega \text{ cm}^2$ )
$r_{\text{H}^+}^a = \frac{\delta_a}{\sigma_{\text{H}^+}^a}$	anode/electrolyte interface proton area specific resistance ( $\Omega \text{ cm}^2$ )
$r_{\text{H}^+}^{\text{el}} = \frac{\ell}{\sigma_{\text{H}^+}^{\text{el}}}$	electrolyte proton area specific resistance ( $\Omega \text{ cm}^2$ )
$I_{\text{O}_2^-}$	oxygen ion current density through the membrane ( $\text{A cm}^{-2}$ )
$I_{\text{H}^+}$	proton current density through the membrane ( $\text{A cm}^{-2}$ )
$I_e$	electronic current density through the membrane ( $\text{A cm}^{-2}$ )
$I_L$	load current (as current density) ( $\text{A cm}^{-2}$ )
$R_e = r_e^c + r_e^{\text{el}} + r_e^a$	electron area specific resistance of the membrane ( $\Omega \text{ cm}^2$ )
$R_{\text{O}_2^-} = r_{\text{O}_2^-}^c + r_{\text{O}_2^-}^{\text{el}} + r_{\text{O}_2^-}^a$	oxygen ion area specific resistance of the membrane ( $\Omega \text{ cm}^2$ )
$R_{\text{H}^+} = r_{\text{H}^+}^c + r_{\text{H}^+}^{\text{el}} + r_{\text{H}^+}^a$	proton area specific resistance of the membrane ( $\Omega \text{ cm}^2$ )
$X = R_{\text{H}^+} R_e + R_{\text{O}_2^-} R_e + R_{\text{H}^+} R_{\text{O}_2^-}$	( $\Omega^2 \text{ cm}^4$ )
$R_L$	load (given as area specific load) ( $\Omega \text{ cm}^2$ )
$R_e' = \frac{R_e R_L}{(R_e + R_L)}$	net electronic area specific resistance including internal electronic resistance and load ( $\Omega \text{ cm}^2$ )
$X' = R_{\text{H}^+} R_e' + R_{\text{O}_2^-} R_e' + R_{\text{H}^+} R_{\text{O}_2^-}$	( $\Omega^2 \text{ cm}^4$ )
$p_{\text{O}_2}$	oxygen partial pressure
$p_{\text{H}_2}$	hydrogen partial pressure
$p_{\text{H}_2\text{O}}$	partial pressure of $\text{H}_2\text{O}$
$R$	ideal gas constant ( $\text{J mol}^{-1} \text{ K}^{-1}$ )
$k_B$	Boltzmann constant ( $\text{J K}^{-1}$ )
$T$	absolute temperature (K)
$F$	Faraday constant ( $\text{C mol}^{-1}$ )
$z_i$	valence of species $i$
$e$	electronic charge (C)
$E_{\text{O}_2}$	Nernst voltage related to differences in $\mu_{\text{O}_2}$ across the membrane (V)
$E_{\text{H}_2}$	Nernst voltage related to differences in $\mu_{\text{H}_2}$ across the membrane (V)
$J_{\text{O}_2}$	flux of $\text{O}_2$ through the membrane ( $\text{mol s}^{-1} \text{ cm}^{-2}$ )
$J_{\text{H}_2}$	flux of $\text{H}_2$ through the membrane ( $\text{mol s}^{-1} \text{ cm}^{-2}$ )
$J_{\text{O}_2^-}$	flux of oxygen ions through the membrane ( $\text{mol s}^{-1} \text{ cm}^{-2}$ )
$J_{\text{H}^+}$	flux of protons through the membrane ( $\text{mol s}^{-1} \text{ cm}^{-2}$ )
$L_{ij}$	Onsager coefficient ( $\text{mol}^2 \text{ cm}^{-2} \text{ s}^{-1} \text{ J}^{-1}$ )

### Greek letters

$\sigma_e^c$	cathode/electrolyte interface electronic conductivity ( $\text{S cm}^{-1}$ )
$\sigma_e^a$	anode/electrolyte interface electronic conductivity ( $\text{S cm}^{-1}$ )
$\sigma_e^{\text{el}}$	electrolyte electronic conductivity ( $\text{S cm}^{-1}$ )
$\sigma_{\text{O}_2^-}^c$	cathode/electrolyte interface oxygen ion conductivity ( $\text{S cm}^{-1}$ )
$\sigma_{\text{O}_2^-}^a$	anode/electrolyte interface oxygen ion conductivity ( $\text{S cm}^{-1}$ )
$\sigma_{\text{O}_2^-}^{\text{el}}$	electrolyte oxygen ion conductivity ( $\text{S cm}^{-1}$ )
$\sigma_{\text{H}^+}^c$	cathode/electrolyte interface proton conductivity ( $\text{S cm}^{-1}$ )
$\sigma_{\text{H}^+}^a$	anode/electrolyte interface proton conductivity ( $\text{S cm}^{-1}$ )
$\sigma_{\text{H}^+}^{\text{el}}$	electrolyte proton conductivity ( $\text{S cm}^{-1}$ )
$\delta_c$	cathode/electrolyte interface thickness (cm)
$\delta_a$	anode/electrolyte interface thickness (cm)
$\mu_{\text{O}_2}$	chemical potential of oxygen ( $\text{J mol}^{-1}$ )
$\mu_{\text{H}_2}$	chemical potential of hydrogen ( $\text{J mol}^{-1}$ )
$\mu_{\text{H}_2\text{O}}$	chemical potential of $\text{H}_2\text{O}$ ( $\text{J mol}^{-1}$ )
$\mu_e$	chemical potential of electrons ( $\text{J mol}^{-1}$ )
$\Phi$	electrostatic potential (V)
$\tilde{\mu}_i = \mu_i + z_i e \Phi$	electrochemical potential of species $i$ ( $\text{J mol}^{-1}$ )
$\varphi = -\frac{\tilde{\mu}_e}{F} = -\frac{\mu_e}{F} + \Phi$	electric potential (V)

and



with local equilibria given by

$$\mu_M = \mu_{M^{n+}} + n\mu_e = \tilde{\mu}_{M^{n+}} + n\tilde{\mu}_e \quad (6)$$

and

$$\mu_X + m\tilde{\mu}_e = \tilde{\mu}_{X^{m-}} \quad (7)$$

where  $\mu_e$  and  $\tilde{\mu}_e$  are respectively chemical and electrochemical potentials of electrons. The  $\mu_e$  in an aqueous solution is a well defined quantity even if the actual concentration of electrons may be negligible so that negligible current is carried by electrons. By virtue of the presence of mobile cations and anions, explicit incorporation of electron/hole chemical potentials is generally not required. Many high temperature materials, however, exhibit substantial mobility for typically only one species. For example, high temperature cubic phase of  $\text{ZrO}_2$  stabilized with  $\text{Y}_2\text{O}_3$  exhibits significant oxygen ion conduction (via a vacancy mechanism) above about  $400^\circ\text{C}$ . Yttrium ( $\text{Y}^{3+}$ ) and zirconium ( $\text{Zr}^{4+}$ ) ions are essentially 'frozen' in place and exhibit no detectable conductivity [3]. Description of local equilibrium in these materials with respect to transporting oxygen ions requires the incorporation of electronic defects – electrons or holes. For example, in an oxygen ion conductor with negligible mobility for cations, local equilibrium reaction may be given by



with local equilibrium given by

$$\frac{1}{2}\mu_{\text{O}_2} + 2\tilde{\mu}_e = \tilde{\mu}_{\text{O}_2^-} \quad (9)$$

Local equilibrium between oxygen ions, neutral oxygen and electrons (holes) is generally assumed regardless how low might be the

electronic conductivity, which is still much greater than ionic conduction of  $Y^{3+}$  and  $Zr^{4+}$ . There are a number of solid state oxygen ion, fluoride ion, chloride ion, sodium ion, lithium ion, potassium ion, and silver ion conductors in which only one mobile ion exists. In all such materials, local equilibrium must be written in terms of electrons (holes). This is an important difference between the extensively investigated aqueous electrolyte solutions and solid electrolytes, and yet often ignored in studies on solid electrolytes [4].

There are many alkaline earth perovskite oxides (e.g. Y-doped  $BaCeO_3$ ) which are predominantly oxygen ion and/or electron hole conductors in a dry atmosphere [5]. When heated in water vapor, they dissolve water thus becoming proton conductors [5]. Such materials thus can transport two ionic species ( $H^+$  and  $O^{2-}$ ) in addition to electrons/holes. Potential applications of these materials are in intermediate temperature (400–700 °C) fuel cells, electrolyzers, and hydrogen separators.

Transport through membranes when multiple species exhibit significant mobilities has been extensively addressed in biological systems. In such systems, significant swelling of the membrane occurs. Many reported works address this aspect by accounting for various frames of reference. In the oxide materials considered here, cation immobility implies rigid lattice and thus a fixed frame of reference. Analysis of transport in biological systems has been examined using what is known as ‘network thermodynamics’ in which analogies between electrical circuits and transport through membranes are drawn [6]. Using this approach, various parameters such as resistances and capacitances can be given in terms of transport parameters of the membrane and thermodynamics of the materials/systems.

In this manuscript, an equivalent circuit approach is used to examine transport through mixed proton, oxygen ion, and electron (hole) conducting membranes under steady state fuel cell conditions. Local equilibrium is assumed in an otherwise non-equilibrium state [7]. Thus, the present analysis is part of the general topic of non-equilibrium steady state [8,9]. By virtue of the assumption of steady state, no changes in ‘capacity’ occur. Thus, the equivalent circuit can be fully described in terms of various resistances and internal EMFs, the latter related to the chemical potentials of the various neutral species. This allows for a complete description of steady state in terms of thermodynamic potentials and dissipative components.

## 2. Analysis

We consider a solid dense membrane (no porosity in the membrane) capable of transporting protons ( $H^+$ ), oxygen ions ( $O^{2-}$ ), and electrons (e) or electron holes (h). Transport of electrons or holes will be treated in terms of a single electronic conductivity which embodies transport of either or both electronic species. Two porous electrodes, cathode and anode, are applied on the two surfaces of the membrane. A mixture of gaseous  $O_2$  and  $H_2O$  is supplied at the cathode and a mixture of gaseous  $H_2$  and  $H_2O$  is supplied at the anode. An external load is connected across the cathode and the anode. Fig. 1 shows a schematic. Cathode/membrane (c) and anode/membrane (a) interfaces are each characterized by three sets of area specific resistances (in  $\Omega \text{ cm}^2$ )—one set for the transfer of  $H^+$  across the interfaces ( $r_{H^+}^c, r_{H^+}^a$ ), one set for the transfer of  $O^{2-}$  across the interfaces ( $r_{O^{2-}}^c, r_{O^{2-}}^a$ ), and one set for the transfer of electrons/holes across the interfaces ( $r_e^c, r_e^a$ ).<sup>2</sup> Area specific resistances for ion transfer across interfaces can be given in terms of

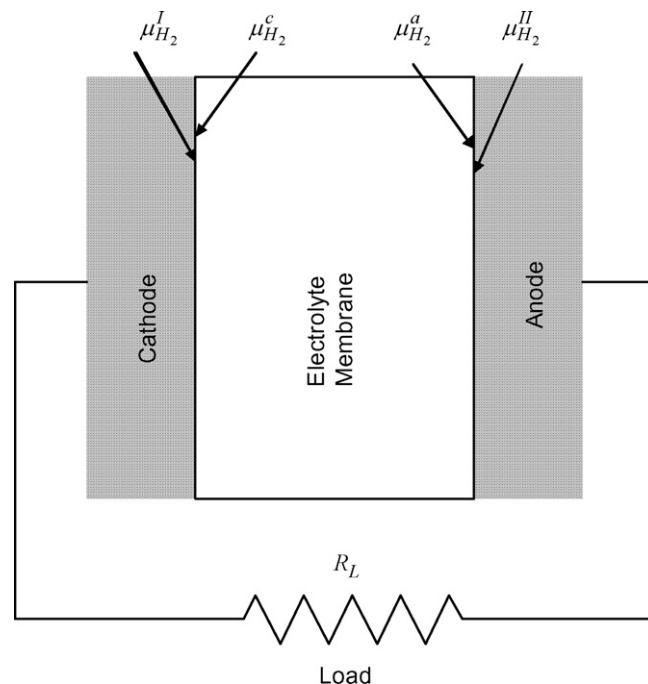


Fig. 1. A schematic of a fuel cell. The locations of the chemical potentials of  $H_2$  just inside the electrolyte ( $\mu_{H_2}^c, \mu_{H_2}^a$ ) and just across into the electrodes ( $\mu_{H_2}^I, \mu_{H_2}^{II}$ ) are labeled in the schematic. The same applies to the other chemical potentials, electrochemical potentials and  $\varphi$ .

fundamental charge transfer mechanisms and may be described phenomenologically by models such as the Butler–Volmer model. Area specific resistances for electron transport across interfaces ( $r_e^c, r_e^a$ ) are measures of direct electron transfer between the electrodes and the electrolyte. For many situations, electron transport through the electrolyte (and across interfaces) is negligible. However, it is not mathematically zero. This means  $r_e^c, r_e^a$  may be very large, but are not infinite [10]. Transport through the membrane is characterized by area specific resistances for  $H^+$  transport,  $O^{2-}$  transport, and electron/hole transport through the membrane. These can be given in terms of the respective bulk conductivities.

Local equilibrium gives for all regions of the membrane and the adjacent gas phases the following relations:



which gives

$$\mu_{H_2} + \frac{1}{2}\mu_{O_2} = \mu_{H_2O} \quad (11)$$



which gives

$$\frac{1}{2}\mu_{H_2} = \tilde{\mu}_{H^+} + \tilde{\mu}_e \quad (13)$$

and Eqs. (8) and (9) describe local equilibrium for oxygen. The above (local) equilibria exist everywhere in the system, including the dense membrane. An important point to note is that chemical potentials of gaseous species are defined in fully dense membranes (no/negligible porosity in the bulk of the membrane) even when the amount of species existing as gas within the solid is negligible (or mathematically zero) [11,12].

At the gas phase/electrolyte (membrane) interface I, on the gas phase side of the interface, local equilibrium gives

$$\mu_{H_2}^I + \frac{1}{2}\mu_{O_2}^I = \mu_{H_2O}^I \quad (14)$$

<sup>2</sup> The interfacial resistances defined here do not include extended electrochemical zones of porous electrodes.

Let I be the cathode. Then, it is understood that for a fuel cell, the cathode predominantly has  $O_2$  and  $H_2O$ , but very little  $H_2$ ; that is  $p_{O_2}, p_{H_2O} \gg p_{H_2}$ . At the gas phase/electrolyte (membrane) interface II, on the gas phase side of the interface, local equilibrium gives

$$\mu_{H_2}^I + \frac{1}{2}\mu_{O_2}^I = \mu_{H_2O}^I \quad (15)$$

Let II be the anode. Then, it is understood that for a fuel cell, the anode predominantly has  $H_2$  and  $H_2O$ , but very little  $O_2$ ; that is  $p_{H_2}, p_{H_2O} \gg p_{O_2}$ .

Local equilibrium *inside the electrolyte* (membrane), just under the cathode/electrolyte interface, is given by

$$\mu_{H_2}^c + \frac{1}{2}\mu_{O_2}^c = \mu_{H_2O}^c \quad (16)$$

Local equilibrium *inside the electrolyte* (membrane), just under the anode/electrolyte interface, is given by

$$\mu_{H_2}^a + \frac{1}{2}\mu_{O_2}^a = \mu_{H_2O}^a \quad (17)$$

The general transport equation for a charged species is

$$I_i = -\frac{\sigma_i}{z_i F} \nabla \tilde{\mu}_i \quad (18)$$

where  $\sigma_i$  is the conductivity due to species  $i$  and  $I_i$  is the current density due to the transport of species  $i$ . This gives

$$I_{H^+} = -\frac{\sigma_{H^+}}{F} \nabla \tilde{\mu}_{H^+} = -\frac{\sigma_{H^+}}{2F} \nabla \mu_{H_2} - \sigma_{H^+} \nabla \varphi \quad (19)$$

$$I_{O^{2-}} = \frac{\sigma_{O^{2-}}}{2F} \nabla \tilde{\mu}_{O^{2-}} = \frac{\sigma_{O^{2-}}}{4F} \nabla \mu_{O_2} - \sigma_{O^{2-}} \nabla \varphi \quad (20)$$

$$I_e = \frac{\sigma_e}{F} \nabla \tilde{\mu}_e = -\sigma_e \nabla \varphi \quad (21)$$

where

$$\varphi = -\frac{\tilde{\mu}_e}{F} = -\frac{\mu_e}{F} + \Phi \quad (22)$$

An important point to note is that what one experimentally measures using a metal wire probe is  $\varphi$  (electric potential) and not the electrostatic potential,  $\Phi$ . Much of the literature on aqueous electrochemistry only refers to the electrostatic potential,  $\Phi$  [13].

For the interface at I, the various area specific resistances ( $\Omega \text{ cm}^2$ ) are as follows:

$$r_{H^+}^c = \frac{\delta_c}{\sigma_{H^+}^c} \quad (23a)$$

$$r_{O^{2-}}^c = \frac{\delta_c}{\sigma_{O^{2-}}^c} \quad (23b)$$

and

$$r_e^c = \frac{\delta_c}{\sigma_e^c} \quad (23c)$$

where  $\delta_c$  is the cathode/electrolyte interface thickness (which could be in the nanometer or fractions of a nanometer range and the interfacial region need not be physically distinct), and  $\sigma_{H^+}^c$ ,  $\sigma_{O^{2-}}^c$  and  $\sigma_e^c$  are respectively proton, oxygen ion and electronic conductivities of the cathode/electrolyte interface. Although the exact character and the thickness of the interface are not readily subject to independent experimental determination, some important features are as follows. The interface region should include one (or few) atomic layers of the solid and one (or few) layers of the gas phase (possibly adsorbed). The surface layer of the solid must always be 'different' from the bulk region due to the presence of unsatisfied bonds. Thus, through this region, the transport properties must also in general be different from the bulk. Similarly, the adsorbed layer will also have different properties than the gas phase. In this discussion, the thickness of this interface is meant to include this transition region (a few

atomic layers thick) which is different from both the solid and the gas phases. Indeed, similar approach has also been used to describe interfaces between liquid and vapor using non-equilibrium molecular dynamics simulations [14]. The interface defined here does not include relatively long range effects such as the space charge, which can be readily included separately.

Similarly, for the anode/electrolyte interface (II), the area specific resistances are

$$r_{H^+}^a = \frac{\delta_a}{\sigma_{H^+}^a} \quad (24a)$$

$$r_{O^{2-}}^a = \frac{\delta_a}{\sigma_{O^{2-}}^a} \quad (24b)$$

and

$$r_e^a = \frac{\delta_a}{\sigma_e^a} \quad (24c)$$

where  $\delta_a$  is the anode/electrolyte interface thickness, and  $\sigma_{H^+}^a$ ,  $\sigma_{O^{2-}}^a$  and  $\sigma_e^a$  are respectively proton, oxygen ion and electronic conductivities of the anode/electrolyte interface. In general, even though the interface conductivities and thicknesses are not separately measurable, interface area specific resistances can be measured, at least in principle, using techniques such as impedance spectroscopy.

Finally, for the bulk electrolyte membrane, the area specific resistances are

$$r_{H^+}^{\text{el}} = \frac{\ell}{\sigma_{H^+}^{\text{el}}} \quad (25a)$$

$$r_{O^{2-}}^{\text{el}} = \frac{\ell}{\sigma_{O^{2-}}^{\text{el}}} \quad (25b)$$

and

$$r_e^{\text{el}} = \frac{\ell}{\sigma_e^{\text{el}}} \quad (25c)$$

where  $\ell$  is the membrane thickness, and  $\sigma_{H^+}^{\text{el}}$ ,  $\sigma_{O^{2-}}^{\text{el}}$  and  $\sigma_e^{\text{el}}$  are respectively proton, oxygen ion and electronic conductivities of the membrane. These in principle can be separately measured and are typically functions of composition (defect chemistry), atmosphere and temperature. For example, oxygen ion conductivity,  $\sigma_{O^{2-}}^{\text{el}}$ , may be given in terms of the oxygen vacancy concentration and the oxygen vacancy diffusivity (mobility). An example is

$$\sigma_{O^{2-}}^{\text{el}} = 4e^2 \frac{D_{V_O^{\bullet\bullet}}}{k_B T} [V_O^{\bullet\bullet}] \quad (26)$$

where  $e$  is the electronic charge,  $D_{V_O^{\bullet\bullet}}$  is the oxygen vacancy diffusivity and  $[V_O^{\bullet\bullet}]$  is the oxygen vacancy concentration. Defect chemistry relations can be readily given for specific cases for all species. These are material and atmosphere dependent. The following discussion is applicable regardless of the details of defect chemistry. For this reason, no particular defect mechanism is assumed in what follows.

Integration and rearrangement of Eqs. (19) through (21) (for a one dimensional case) assuming transport parameters are constant, independent of position, gives

$$\begin{aligned} \mu_{O_2}^c &= \mu_{O_2}^I + 4F \{ r_{O^{2-}}^c I_{O^{2-}} - r_e^c I_e \} \\ &= \mu_{O_2}^I + 4F r_{O^{2-}}^c I_{O^{2-}} - 4F \{ \varphi^I - \varphi^c \} \end{aligned} \quad (27)$$

$$\begin{aligned} \mu_{H_2}^c &= \mu_{H_2}^I - 2F \{ r_{H^+}^c I_{H^+} - r_e^c I_e \} \\ &= \mu_{H_2}^I - 2F r_{H^+}^c I_{H^+} + 2F \{ \varphi^I - \varphi^c \} \end{aligned} \quad (28)$$

and

$$\varphi^c = \varphi^I - r_e^c I_e \quad (29)$$

where all thermodynamic potentials ( $\mu$ s and  $\varphi$ ) with superscript *c* refer to values in the membrane just inside the cathode/electrolyte interface.

Similarly, for the anode/electrolyte interface (just inside the membrane)

$$\begin{aligned} \mu_{O_2}^a &= \mu_{O_2}^l - 4F \{ r_{O_2^-}^a I_{O_2^-} - r_e^a I_e \} \\ &= \mu_{O_2}^l - 4Fr_{O_2^-}^a I_{O_2^-} + 4F \{ \varphi^a - \varphi^l \} \end{aligned} \quad (30)$$

$$\begin{aligned} \mu_{H_2}^a &= \mu_{H_2}^l + 2F \{ r_{H^+}^a I_{H^+} - r_e^a I_e \} \\ &= \mu_{H_2}^l + 2Fr_{H^+}^a I_{H^+} - 2F \{ \varphi^a - \varphi^l \} \end{aligned} \quad (31)$$

and

$$\varphi^a = \varphi^l + r_e^a I_e \quad (32)$$

where all thermodynamic potentials ( $\mu$ s and  $\varphi$ ) with superscript *a* refer to values in the membrane just inside the anode/electrolyte interface.

Eqs. (27) through (32) describe thermodynamic potentials *within* the electrolyte, just under the electrode/electrolyte interfaces. The most important feature of these equations is that they describe thermodynamic potentials in terms of ionic and electronic currents. Thus, by virtue of the presence of terms containing products of electronic resistances and electronic currents, that is of the type  $r_e^a I_e$  and  $r_e^c I_e$ , it is to be noted that one *cannot* a-priori assume electronic resistances as being infinite (that is  $r_e^a \neq \infty$  and  $r_e^c \neq \infty$ ), as is commonly done. This is because if the electronic resistance is infinite, then  $I_e$  will go to zero resulting in indeterminate terms ( $\infty \times 0$ ) in Eqs. (27) through (32), making thermodynamic potentials indeterminate—and thus violating local equilibrium [7,12]. Based on considerable work done on non-equilibrium thermodynamics, it is now well established that local equilibrium is applicable in virtually all practical systems of interest, such as the one considered here. Thus, local equilibrium must be valid—which here means electronic resistance cannot be assumed to be infinite.

### 2.1. The equivalent circuit

An equivalent circuit describing steady state transport can be constructed for each of the segments. This is described in what follows.

#### 2.1.1. The cathode/electrolyte interface segment

Rearrangement of Eq. (28) for the change in chemical potential of  $H_2$  across the cathode/electrolyte interface gives

$$\frac{\mu_{H_2}^c - \mu_{H_2}^l}{2F} + r_{H^+}^c I_{H^+} = \varphi^l - \varphi^c = r_e^c I_e \quad (33)$$

Note that  $\varphi^l - \varphi^c = r_e^c I_e$  is the ‘voltage’ drop or ‘electric potential’ drop across the cathode/electrolyte interface. Write

$$E_{H_2}^c = \frac{\mu_{H_2}^c - \mu_{H_2}^l}{2F} > 0 \quad (34)$$

Note this is the Nernst potential which relates the change in free energy of transferring one mole of hydrogen from *c* to *l* (cathode).

Thus,

$$E_{H_2}^c + r_{H^+}^c I_{H^+} = r_e^c I_e = \varphi^l - \varphi^c \quad (35)$$

Similarly,

$$\frac{\mu_{O_2}^l - \mu_{O_2}^c}{4F} + r_{O_2^-}^c I_{O_2^-} = \varphi^l - \varphi^c = r_e^c I_e \quad (36)$$

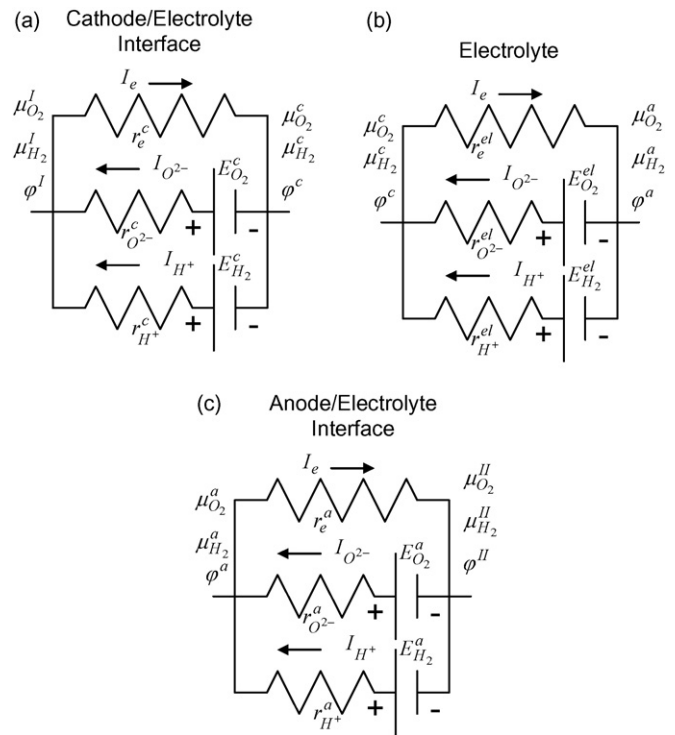


Fig. 2. Equivalent circuits for the cathode/electrolyte interface (a), the electrolyte (b), and electrolyte/anode interface (c).

Write

$$E_{O_2}^c = \frac{\mu_{O_2}^l - \mu_{O_2}^c}{4F} > 0 \quad (37)$$

Note this is the Nernst potential which relates the change in free energy of transferring one mole of oxygen from *l* to *c* (cathode).

Thus,

$$E_{O_2}^c + r_{O_2^-}^c I_{O_2^-} = r_e^c I_e = \varphi^l - \varphi^c \quad (38)$$

Fig. 2(a) shows the equivalent circuit for the cathode/electrode interface portion of the cell. Note that

$$E_{O_2}^c - E_{H_2}^c = \frac{\mu_{H_2O}^l - \mu_{H_2O}^c}{2F} \quad (39)$$

In general the magnitudes of  $E_{H_2}^c$  and  $E_{O_2}^c$  will be different. The only condition for which they would be the same will be if  $\mu_{H_2O}^l = \mu_{H_2O}^c$ , which would be a very unlikely case. In general,  $\mu_{H_2O}^l \neq \mu_{H_2O}^c$ , even when the partial pressures of  $H_2O$  may be the same at the cathode and anode, i.e., even when  $\mu_{H_2O}^l = \mu_{H_2O}^l$  (which would be the case if fuel and oxidant are humidified to the same degree). This aspect will be discussed later.

#### 2.1.2. The electrolyte segment

Similar analysis as above for the electrolyte segment gives

$$\varphi^c - \varphi^a = r_e^{el} I_e \quad (40)$$

For hydrogen,

$$E_{H_2}^{el} = \frac{\mu_{H_2}^a - \mu_{H_2}^c}{2F} > 0 \quad (41)$$

and

$$E_{H_2}^{el} + r_{H^+}^{el} I_{H^+} = r_e^{el} I_e = \varphi^c - \varphi^a \quad (42)$$



For oxygen,

$$E_{O_2}^{el} = \frac{\mu_{O_2}^c - \mu_{O_2}^a}{4F} > 0 \tag{43}$$

and

$$E_{O_2}^{el} + r_{O_2}^{el} I_{O_2} = r_e^{el} I_e = \varphi^c - \varphi^a \tag{44}$$

Note that

$$E_{O_2}^{el} - E_{H_2}^{el} = \frac{\mu_{H_2O}^c - \mu_{H_2O}^a}{2F} \tag{45}$$

In general, the magnitudes of  $E_{H_2}^{el}$  and  $E_{O_2}^{el}$ , are different. Fig. 2(b) shows the equivalent circuit for the electrolyte portion of the cell.

2.1.3. Anode–electrolyte segment

Similar analysis for the electrolyte/anode interface gives

$$\varphi^a - \varphi^{II} = r_e^a I_e \tag{46}$$

For hydrogen

$$E_{H_2}^a = \frac{\mu_{H_2}^{II} - \mu_{H_2}^a}{2F} > 0 \tag{47}$$

and

$$E_{H_2}^a + r_{H_2}^a I_{H_2} = r_e^a I_e = \varphi^a - \varphi^{II} \tag{48}$$

For oxygen

$$E_{O_2}^a = \frac{\mu_{O_2}^a - \mu_{O_2}^{II}}{4F} > 0 \tag{49}$$

and

$$E_{O_2}^a + r_{O_2}^a I_{O_2} = r_e^a I_e = \varphi^a - \varphi^{II} \tag{50}$$

Note that

$$E_{O_2}^a - E_{H_2}^a = \frac{\mu_{H_2O}^a - \mu_{H_2O}^{II}}{2F} \tag{51}$$

In general, the magnitudes of  $E_{H_2}^a$  and  $E_{O_2}^a$ , are different. Fig. 2(c) shows the equivalent circuit for the anode/electrolyte interface portion of the cell.

Equivalent circuit for the complete cell at open circuit is merely a series connection of the three segments. The general case is one where an external load is connected. This is shown in Fig. 3. The various parameters of the equivalent circuit are given in what follows.

2.2. Nernst voltages

The Nernst voltages are given by

$$E_{O_2} = E_{O_2}^c + E_{O_2}^{el} + E_{O_2}^a = \frac{RT}{4F} \ln \left( \frac{p_{O_2}^I}{p_{O_2}^{II}} \right) = \frac{\mu_{O_2}^I - \mu_{O_2}^{II}}{4F} \tag{52}$$

and

$$E_{H_2} = E_{H_2}^c + E_{H_2}^{el} + E_{H_2}^a = \frac{RT}{2F} \ln \left( \frac{p_{H_2}^{II}}{p_{H_2}^I} \right) = \frac{\mu_{H_2}^{II} - \mu_{H_2}^I}{2F} \tag{53}$$

The  $E_{O_2}$  and  $E_{H_2}$  are in general different. They will be equal only if  $\mu_{H_2O}^I = \mu_{H_2O}^{II}$  (that is the same degree of humidification at both electrodes).

2.3. Cell ionic and electronic area specific resistances including membrane/electrode interfaces

The various cell area specific resistances are

$$R_{O_2} = r_{O_2}^c + r_{O_2}^{el} + r_{O_2}^a \tag{54}$$

$$R_{H_2} = r_{H_2}^c + r_{H_2}^{el} + r_{H_2}^a \tag{55}$$

$$R_e = r_e^c + r_e^{el} + r_e^a \tag{56}$$

2.4. The current densities

The various current densities are  $I_{H^+}$ ,  $I_{O_2}$ ,  $I_e$ , and  $I_L$  ( $I_L$  is the load current, given as current density per unit electrode area). In the above the signs of the various current densities (with respect to Figs. 1 and 3, and with the positive direction through the membrane from left to right—from the cathode through the membrane to the anode) are as follows:  $I_{O_2} < 0$ ,  $I_{H^+} < 0$ ,  $I_e > 0$ , and  $I_L < 0$ . The relationship between the current densities is

$$I_L = I_{O_2} + I_{H^+} + I_e \tag{57}$$

In terms of the various resistances and current densities, the cell voltage is given by

$$V = \varphi^I - \varphi^{II} = I_e R_e = -I_L R_L = E_{O_2} + I_{O_2} R_{O_2} = E_{H_2} + I_{H^+} R_{H_2} \tag{58}$$

Analysis of the equivalent circuit shows that the cell voltage,  $V = \varphi^I - \varphi^{II}$  is given by

$$V = \varphi^I - \varphi^{II} = E - |I_L| R_{cell} \tag{59}$$

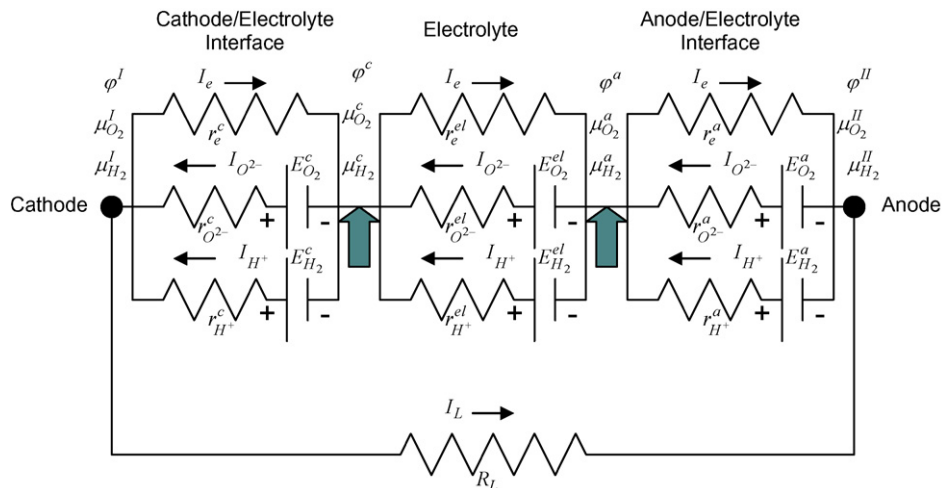


Fig. 3. An equivalent circuit for a fuel cell with a mixed proton, oxygen ion and electron/hole conducting membrane. The block arrows show the locations where the various potentials within the electrolyte, just across electrode/electrolyte interfaces, are defined. The circuit elements between the filled circles at the ends are not physically separable.

where  $|I_L|$  is the magnitude of the load current, the cell open circuit voltage (OCV) is

$$E = \left( \frac{E_{O_2}}{R_{O_2^-}} + \frac{E_{H_2}}{R_{H^+}} \right) \frac{R_{O_2^-} R_{H^+} R_e}{(R_{H^+} R_e + R_{O_2^-} R_e + R_{H^+} R_{O_2^-})} \quad (60)$$

and the cell area specific resistance is

$$R_{cell} = \frac{R_{O_2^-} R_{H^+} R_e}{(R_{H^+} R_e + R_{O_2^-} R_e + R_{H^+} R_{O_2^-})} \quad (61)$$

For convenience of a shortened notation we will write in what follows

$$X = R_{H^+} R_e + R_{O_2^-} R_e + R_{H^+} R_{O_2^-} \quad (62)$$

The short circuit current density is given by

$$|I_{L(s)}| = \left( \frac{E_{O_2}}{R_{O_2^-}} + \frac{E_{H_2}}{R_{H^+}} \right) \quad (63)$$

Both the  $V$  and  $|I_L|$  are functions of the load,  $R_L$ . The power density at any load is simply the product of  $V$  and  $|I_L|$ .

The OCV (Eq. (60)) is effectively the cell potential as defined in the Goldman–Hodgkin–Katz equation [1,2], which is the cell potential (an experimentally measured quantity) in terms of the individual Nernst voltages and transport parameters. In much of the literature on solid electrolytes, the cases on interest involve a single Nernst voltage. An example of a system with two Nernst potentials is described here for a solid electrolyte membrane transporting two ions. In biological/aqueous systems, the GHK equation is given in terms of the properties of the membrane and ignoring the effects of interfaces. If the membrane is thin, however, interface contributions dominate transport resistance through the membrane. Thus, for thin membranes, it is necessary to include interface effects. Eqs. (60) and (61) given here do take into account interface effects and thus are applicable to membranes of any thickness.

For a predominantly  $O_2^-$  conductor with negligible  $H^+$  conduction and negligible electron transport, Eq. (59) reduces to  $V = \varphi^I - \varphi^{II} = E_{O_2} - |I_L| R_{O_2^-}$ . For a predominantly  $H^+$  conductor with negligible  $O_2^-$  conduction and negligible electron conduction, Eq. (59) reduces to  $V = \varphi^I - \varphi^{II} = E_{H_2} - |I_L| R_{H^+}$ . These equations are commonly used when describing a solid oxide fuel cell (SOFC) based on an oxygen ion conductor (e.g. YSZ) [15] or a proton exchange membrane fuel cell (PEMFC) using a proton conductor. Eqs. (58) through (63) and the equivalent circuit describe the behavior of mixed proton, oxygen ion, electron (hole) conducting membranes, such as various doped alkaline earth perovskites (e.g. Y-doped  $BaCeO_3$  or Y-doped  $BaZrO_3$ ). These equations also take into account transport of all three species ( $H^+$ ,  $O_2^-$  and electrons/holes) across electrode/membrane interfaces.

### 2.5. Transport under open circuit condition (OCV)

At OCV, the load current is zero. When the load current is zero ( $|I_L| = 0$ ), that is when the load resistance is infinite, no net current flows through the cell. In such a case,  $I_{O_2^-} + I_{H^+} + I_e = 0$ . Solution to the transport equations for proton and oxygen ion current densities gives,

$$I_{O_2^-} = -\frac{R_e + R_{H^+}}{X} E_{O_2} + \frac{R_e}{X} E_{H_2} \quad (64)$$

and

$$I_{H^+} = \frac{R_e}{X} E_{O_2} - \frac{R_e + R_{O_2^-}}{X} E_{H_2} \quad (65)$$

Eqs. (64) and (65) satisfy Onsager reciprocity relations, as is to be expected. The corresponding electronic current density is given

by<sup>3</sup>

$$I_e = \frac{R_{H^+}}{X} E_{O_2} + \frac{R_{O_2^-}}{X} E_{H_2} \quad (66)$$

The ion fluxes (in  $\text{mol cm}^{-2} \text{s}^{-1}$ ) are related to the current densities as follows:

$$I_{O_2^-} = -2FJ_{O_2^-} \quad (67)$$

and

$$I_{H^+} = FJ_{H^+} \quad (68)$$

There is no net current flowing through the cell. The ion fluxes are equivalent to the corresponding neutral species 'permeation' fluxes. Thus,

$$I_{O_2^-} = -2FJ_{O_2^-} = -4FJ_{O_2} \quad (69)$$

and

$$I_{H^+} = FJ_{H^+} = 2FJ_{H_2} \quad (70)$$

where  $J_{O_2}$  and  $J_{H_2}$  are permeation fluxes of  $O_2$  and  $H_2$  respectively across the membrane (cell).

Eqs. (69) and (70) thus can be rearranged to read

$$J_{O_2} = -\frac{R_e + R_{H^+}}{16F^2X} \Delta\mu_{O_2} - \frac{R_e}{8F^2X} \Delta\mu_{H_2} \quad (71)$$

and

$$J_{H_2} = -\frac{R_e}{8F^2X} \Delta\mu_{O_2} - \frac{R_e + R_{O_2^-}}{4F^2X} \Delta\mu_{H_2} \quad (72)$$

where

$$\Delta\mu_{O_2} = \mu_{O_2}^{II} - \mu_{O_2}^I \quad (73)$$

and

$$\Delta\mu_{H_2} = \mu_{H_2}^{II} - \mu_{H_2}^I \quad (74)$$

Note Eqs. (71) and (72) are of the form

$$J_{O_2} = -L_{O_2O_2} \Delta\mu_{O_2} - L_{O_2H_2} \Delta\mu_{H_2} \quad (75)$$

$$J_{H_2} = -L_{H_2O_2} \Delta\mu_{O_2} - L_{H_2H_2} \Delta\mu_{H_2} \quad (76)$$

where

$$L_{O_2O_2} = \frac{R_e + R_{H^+}}{16F^2X} \quad (77)$$

$$L_{H_2H_2} = \frac{R_e + R_{O_2^-}}{4F^2X} \quad (78)$$

$$L_{H_2O_2} = L_{O_2H_2} = \frac{R_e}{8F^2X} \quad (79)$$

Note that Eqs. (71), (72), (75), and (76) are the Onsager equations and the cross terms satisfy the Onsager reciprocity relations. In these equations, the driving forces are given not as gradients but as differences in chemical potentials across the membrane, that is,  $\Delta\mu_{O_2} = \mu_{O_2}^{II} - \mu_{O_2}^I$  and  $\Delta\mu_{H_2} = \mu_{H_2}^{II} - \mu_{H_2}^I$ . Thus, the  $L_{ij}$ s defined here contain an additional length dimension in the denominator compared to the usual definition [6]. Eq. (79) shows that the reciprocity relations are obeyed not only for the bulk membrane but also include interface transport properties embodied in  $R_{O_2^-}$  (i.e.  $r_{O_2^-}^c, r_{O_2^-}^a$ ),  $R_{H^+}$  (i.e.  $r_{H^+}^c, r_{H^+}^a$ ) and  $R_e$  (i.e.  $r_e^c, r_e^a$ ). It was assumed in the foregoing that transport properties of the membrane are position-independent. If the transport properties do depend on position, the

<sup>3</sup> It is easy to show that if the electrolyte material is a predominantly  $O_2^-$  conductor with negligible  $H^+$  conduction, then  $I_{O_2^-}$  and  $I_e$  are coupled. On the other hand if the electrolyte material is a predominantly  $H^+$  conductor with negligible  $O_2^-$  conduction, then  $I_{H^+}$  and  $I_e$  are coupled.

cell membrane may be discretized into as many segments as needed for any desired level of accuracy [12]. As long as steady state is maintained, equations of the form given in (75) through (79) continue to be valid. Also, interface parameters are naturally included in the transport equations. Thus, the generalized form of Onsager transport equations as given in terms of  $\Delta\mu$ s across the membrane remains valid, inclusive of interface effects even when transport parameters depend upon local composition (and thus on position).

## 2.6. Chemical potentials in the electrolyte just under electrode/electrolyte interfaces

Substitution of the equations for current densities into Eqs. (27), (28), (30), and (31) gives the chemical potentials  $\mu_{O_2}^c$ ,  $\mu_{H_2}^c$ ,  $\mu_{O_2}^a$ , and  $\mu_{H_2}^a$  as follows:

$$\mu_{O_2}^c = \mu_{O_2}^I + 4F \times \left\{ -\frac{[r_{O_2}^c(R_e + R_{H^+}) + r_e^c R_{H^+}]}{X} E_{O_2} + \frac{[r_{O_2}^c R_e - r_e^c R_{O_2}]}{X} E_{H_2} \right\} \quad (80)$$

$$\mu_{H_2}^c = \mu_{H_2}^I - 2F \times \left\{ \frac{[r_{H^+}^c R_e - r_e^c R_{H^+}]}{X} E_{O_2} - \frac{[r_{H^+}^c(R_e + R_{O_2}) + r_e^c R_{O_2}]}{X} E_{H_2} \right\} \quad (81)$$

$$\mu_{O_2}^a = \mu_{O_2}^{II} - 4F \times \left\{ -\frac{[r_{O_2}^a(R_e + R_{H^+}) + r_e^a R_{H^+}]}{X} E_{O_2} + \frac{[r_{O_2}^a R_e - r_e^a R_{O_2}]}{X} E_{H_2} \right\} \quad (82)$$

$$\mu_{H_2}^a = \mu_{H_2}^{II} + 2F \times \left\{ \frac{[r_{H^+}^a R_e - r_e^a R_{H^+}]}{X} E_{O_2} - \frac{[r_{H^+}^a(R_e + R_{O_2}) + r_e^a R_{O_2}]}{X} E_{H_2} \right\} \quad (83)$$

Eqs. (80) through (83) describe chemical potentials of  $O_2$  and  $H_2$  in the electrolyte, just inside the electrode/electrolyte interfaces at OCV in terms of parameters which are measurable experimentally, at least in principle. An important point to note is that in general the terms in ‘{ }’ are not zero. Thus, the chemical potentials must exhibit abrupt changes across interfaces [12,16]. That is, in general,  $\mu_{H_2}^c \neq \mu_{H_2}^I$ ,  $\mu_{H_2}^a \neq \mu_{H_2}^{II}$ ,  $\mu_{O_2}^c \neq \mu_{O_2}^I$  and  $\mu_{O_2}^a \neq \mu_{O_2}^{II}$ .

In many reported works on solid electrolytes, it has been commonly assumed that chemical potentials equilibrate across interfaces. The present work shows that such equilibration is not to be expected. In fact, as shown previously [16], equilibration of chemical potential across interfaces is generally not valid even if the electrode is reversible. That is, reversible electrode does not mean equilibration of the chemical potential of neutral species across electrode/electrolyte interfaces as is often assumed, when there is a finite, nonzero chemical potential difference across the membrane. Indeed, recent work on other systems (vapor/liquid interfaces) using non-equilibrium molecular dynamics simulations has also shown that there are abrupt chemical potential jumps across interfaces [17]. It is easily seen that the  $\phi$  also exhibits abrupt changes across the two interfaces. Fig. 4 shows a schematic of the variation of  $\mu_{H_2}$ ,  $\mu_{O_2}$  and  $\phi$  through the membrane and discontinuous changes across interfaces.

Abrupt changes in chemical potentials and electric potential across interfaces represent a manifestation of the existence of

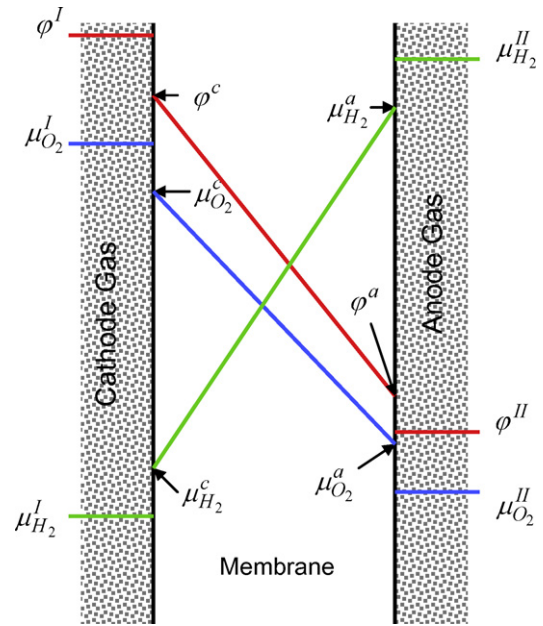


Fig. 4. Schematic variations of  $\mu_{H_2}$ ,  $\mu_{O_2}$ , and  $\phi$ . Discontinuous changes in chemical potentials and electric potential,  $\phi$ , occur across the interfaces in all functions.

rather thin interfacial regions. This means that chemical potentials and electric potential change smoothly within the individual phases (gas and solid), but change abruptly at the interface. Within the interfacial region itself, it is expected that chemical potentials and electric potential vary continuously. The thinner is the interfacial region, the more sharply do the chemical potentials and the electric potential vary within the interfacial region. Thus, on a microscopic scale (micron or a fraction of micron), discontinuous changes in chemical potentials and electric potential occur across interfaces.

Substitution for  $\mu_{O_2}^c$  and  $\mu_{H_2}^c$  in Eq. (16), and  $\mu_{O_2}^a$  and  $\mu_{H_2}^a$  in Eq. (17) gives the corresponding chemical potentials of  $H_2O$  in the electrolyte, just under the electrode/electrolyte interfaces, namely,

$$\mu_{H_2O}^c = \mu_{H_2O}^I - 2F \left\{ \frac{[r_{H^+}^c R_e + r_{O_2}^c(R_e + R_{H^+})]}{X} E_{O_2} - \frac{[r_{H^+}^c(R_e + R_{O_2}) + r_{O_2}^c R_e]}{X} E_{H_2} \right\} \quad (84)$$

$$\mu_{H_2O}^a = \mu_{H_2O}^{II} + 2F \left\{ \frac{[r_{H^+}^a R_e + r_{O_2}^a(R_e + R_{H^+})]}{X} E_{O_2} - \frac{[r_{H^+}^a(R_e + R_{O_2}) + r_{O_2}^a R_e]}{X} E_{H_2} \right\} \quad (85)$$

Eqs. (84) and (85) show that the chemical potential of  $H_2O$  must also exhibit abrupt changes across interfaces since in general terms in ‘{ }’ are nonzero. This result also shows further interesting features. Suppose both the cathode and the anode are humidified to the same degree, that is suppose  $\mu_{H_2O}^I = \mu_{H_2O}^{II}$ . Even then,  $\mu_{H_2O}^c \neq \mu_{H_2O}^a$ . This means there will be a gradient in  $\mu_{H_2O}$  through the membrane even when the same partial pressure of  $H_2O$  exists in the two gas phases (cathode and anode).

## 2.7. Currents under load

When an external load is connected so that a finite current ( $I_L$ ) flows through the external circuit, oxygen ion and proton current



densities are given by

$$I_{O_2^-} = -\frac{R_e + R_{H^+}}{X} E_{O_2} + \frac{R_e}{X} E_{H_2} + \frac{R_{H^+} R_e}{X} I_L \tag{86}$$

and

$$I_{H^+} = \frac{R_e}{X} E_{O_2} - \frac{R_e + R_{O_2^-}}{X} E_{H_2} + \frac{R_{O_2^-} R_e}{X} I_L \tag{87}$$

Eqs. (86) and (87) can also be written in terms of the load resistance,  $R_L$ , as

$$I_{O_2^-} = -\frac{R'_e + R_{H^+}}{X'} E_{O_2} + \frac{R'_e}{X'} E_{H_2} \tag{88}$$

and

$$I_{H^+} = \frac{R'_e}{X'} E_{O_2} - \frac{R'_e + R_{O_2^-}}{X'} E_{H_2} \tag{89}$$

where we have written

$$R'_e = \frac{R_e R_L}{R_e + R_L} \tag{90}$$

which is the net electronic area specific resistance, including the external load. Also,

$$X' = R_{H^+} R'_e + R_{O_2^-} R'_e + R_{H^+} R_{O_2^-} \tag{91}$$

Note that Eqs. (88) and (89) are similar to Eqs. (64) and (65) and satisfy the Onsager reciprocity relations. Fluxes of  $O_2$  and  $H_2$  are also similar to Eqs. (71) and (72) with  $R_e$  replaced by  $R'_e$ , and  $X$  replaced by  $X'$ , and are given by

$$J_{O_2} = -\frac{R'_e + R_{H^+}}{16F^2 X'} \Delta\mu_{O_2} - \frac{R'_e}{8F^2 X'} \Delta\mu_{H_2} \tag{92}$$

and

$$J_{H_2} = -\frac{R'_e}{8F^2 X'} \Delta\mu_{O_2} - \frac{R'_e + R_{O_2^-}}{4F^2 X'} \Delta\mu_{H_2} \tag{93}$$

Eqs. (92) and (93) can still be considered as ‘permeation’ fluxes wherein part of the coupling electron flux is through the external load. That is, Eqs. (92) and (93) represent permeation fluxes for the combined system comprising the cell and the load. The corresponding transport coefficients are the same as Eqs. (77) through (79) with  $R_e$  replaced by  $R'_e$  and  $X$  replaced by  $X'$ , namely

$$L'_{O_2 O_2} = \frac{R'_e + R_{H^+}}{16F^2 X'} \tag{94}$$

$$L'_{H_2 H_2} = \frac{R'_e + R_{O_2^-}}{4F^2 X'} \tag{95}$$

$$L'_{H_2 O_2} = L'_{O_2 H_2} = \frac{R'_e}{8F^2 X'} \tag{96}$$

Finally, it is easily seen that

$$L'_{O_2 O_2} L'_{H_2 H_2} - (L'_{H_2 O_2})^2 \geq 0 \tag{97}$$

as required [18].

Various limiting cases of the above equations can be examined, all satisfying Onsager reciprocity equations. In the short circuit limit,  $R'_e = 0$ , for which

$$L'_{H_2 O_2} = L'_{O_2 H_2} = 0 \tag{98}$$

That is, there is no coupling between  $H_2$  and  $O_2$  fluxes at short circuit. Consider now  $R'_e \rightarrow \infty$ , i.e. no load applied and negligible electronic conduction through the membrane. Then the corresponding transport parameters are

$$L'_{O_2 O_2} = \frac{1}{16F^2 (R_{H^+} + R_{O_2^-})} \tag{99}$$

$$L'_{H_2 H_2} = \frac{1}{4F^2 (R_{H^+} + R_{O_2^-})} \tag{100}$$

and

$$L'_{O_2 H_2} = L'_{H_2 O_2} = \frac{1}{8F^2 (R_{H^+} + R_{O_2^-})} \tag{101}$$

In this case, the origin of coupling is purely ionic. In such a case

$$L'_{O_2 O_2} L'_{H_2 H_2} - (L'_{H_2 O_2})^2 = 0 \tag{102}$$

Thus, the degree of coupling between  $H_2$  and  $O_2$  transport through the membrane is a function of the net electronic resistance (including internal and external) and varies between no coupling for zero electronic resistance to maximum coupling for infinite electronic resistance.

The chemical potentials of  $H_2$ ,  $O_2$ , and  $H_2O$  in the electrolyte, just under the electrode/electrolyte interfaces, are the same as (80)–(85) with  $R_e$  replaced by  $R'_e$  which includes the load resistance,  $R_L$  (thus also replacing  $X$  by  $X'$ ).

### 2.8. Significance of equations describing chemical potentials inside the electrolyte as a function of various current densities and transport parameters

Eqs. (80) through (83) describe chemical potentials of  $O_2$  and  $H_2$  in terms of the various current densities ( $I_{O_2^-}$ ,  $I_{H^+}$ , and  $I_e$ ) and transport parameters at OCV. The same equations are applicable under load with  $R_e$  replaced by  $R'_e$  and  $X$  replaced by  $X'$ . A key point to note is that recognition and incorporation of local equilibrium has made it possible to determine chemical potentials of neutral species within the electrolyte. These equations show that for a single fuel cell, since the ionic current densities ( $I_{O_2^-}$  and  $I_{H^+}$ ) are in the opposite direction to the electronic current density ( $I_e$ ), the  $\mu_{H_2}$  and  $\mu_{O_2}$  in the electrolyte are always mathematically bounded by values at the electrodes (that is by  $\mu_{H_2}^I$  and  $\mu_{H_2}^{II}$ ; and by  $\mu_{O_2}^I$  and  $\mu_{O_2}^{II}$ ) [12]. However, when many cells are connected in series, in an unbalanced cell the ionic and electronic currents can be in the same direction (the electronic current changes direction). In such a case, the chemical potentials of  $H_2$  and  $O_2$  within the electrolyte are not mathematically bounded. There are some situations in which stack failure can occur as described previously [16,19].

### 2.9. Possible experimental procedure for the verification of the transport equations

The analysis given here assumes that the transport parameters ( $R_{O_2^-}$ ,  $R_{H^+}$  and  $R_e$ ) are independent of gas phase compositions and of the net current transporting through the membrane. In many experimental situations, this may not be the case. Nevertheless, if this assumption is approximately valid, an experimental approach can be envisioned for the measurement of transport parameters. In what follows, this is illustrated using Eqs. (92) and (93).

The approach consists of applying a known load ( $R_L$ ) across the cell. The cathode is exposed to a mixture of  $O_2$  and  $H_2O$ . The anode is exposed to a mixture of  $H_2$  and  $H_2O$ . The corresponding chemical potential differences of  $O_2$  and  $H_2$ , namely  $\Delta\mu_{O_2}$  and  $\Delta\mu_{H_2}$ , can be determined based on the compositions (partial pressures) of the gases. By conducting chemical analysis of incoming and exiting gases at the two electrodes and measuring gas flow rates, the net fluxes of  $O_2$  and  $H_2$ , namely  $J_{O_2}$  and  $J_{H_2}$ , can be experimentally measured as a function of the imposed  $\Delta\mu_{O_2}$  and  $\Delta\mu_{H_2}$ . Then, the gas mixtures of the two electrodes are changed such that only one of the chemical potential differences is altered at a time. For example, consider changing  $\Delta\mu_{O_2}$  but keeping  $\Delta\mu_{H_2}$  fixed. The net fluxes of  $O_2$  and  $H_2$ , namely  $J_{O_2}$  and  $J_{H_2}$ , are again measured. This procedure is repeated for various values of  $\Delta\mu_{O_2}$  for a fixed value of  $\Delta\mu_{H_2}$ . The rate of change  $J_{O_2}$  as a function of  $\Delta\mu_{O_2}$  for a fixed  $\Delta\mu_{H_2}$  gives

$L'_{O_2O_2}$  (Eq. (94)). Similarly, the rate of change of  $J_{H_2}$  as a function of  $\Delta\mu_{O_2}$  for a fixed  $\Delta\mu_{H_2}$  gives  $L'_{H_2O_2}$ .

A similar series of experiments is conducted wherein the  $\Delta\mu_{H_2}$  is systematically varied while fixing  $\Delta\mu_{O_2}$ . In this case, the rate of change of  $J_{O_2}$  as a function of  $\Delta\mu_{H_2}$  for a fixed  $\Delta\mu_{O_2}$  gives  $L'_{O_2H_2}$  and the rate of change of  $J_{H_2}$  as a function of  $\Delta\mu_{H_2}$  for a fixed  $\Delta\mu_{O_2}$  gives  $L'_{H_2H_2}$  (Eq. (95)). The  $L'_{H_2O_2}$  and  $L'_{O_2H_2}$  determined from the two sets of experiments should be equal to each other and given by Eq. (96). The above describes a possible experimental approach for verification and general application of the equations derived here, and for the verification of Onsager reciprocity relations for transport through mixed  $O^{2-}$ ,  $H^+$ , and electron (hole) conductors. From these measurements, transport parameters for the membrane, namely,  $R_{O^{2-}}$ ,  $R_{H^+}$ , and  $R_e$  can be determined.

### 3. Summary

The present manuscript has examined steady state transport through mixed proton, oxygen ion, and electron (hole) conductors. Transport through membranes in a fuel cell mode was examined. Transport properties of all transporting species ( $H^+$ ,  $O^{2-}$ , e or h) across cathode/electrolyte and anode/electrolyte interfaces were incorporated into the analysis and a simple equivalent circuit was presented. Only steady state was examined. This allowed for the use of an equivalent circuit in terms of internal EMFs (measures of chemical potential differences) and resistors (dissipative components), without the need for elements describing 'capacity'. Ion transport properties across interfaces are measures of electrochemical charge transfer reactions at the physically sharp electrode/electrolyte interfaces (not including the extended porous electrode). Electron transport properties across interfaces are measures of direct electron transfer between the electrodes and the electrolyte. The open circuit voltage of cell/membrane is given in terms of chemical potentials of  $H_2$  and  $O_2$  at the two electrodes and transport properties of the membrane including interfaces. The resulting equation is similar to the Goldman–Hodgkin–Katz equation used in cell physiology describing ion transport across cell walls. Transport through the membrane, inclusive of interface transport properties, obeys Onsager relations. In many situations, membranes can be very thin. In such cases, interface effects dominate transport. The present analysis shows that Onsager reciprocity relations are valid with interface parameters included in the transport equations. In the analysis, transport properties through the

bulk membrane were assumed to be position-independent. If they are position-dependent, the entire cell can be discretized into as many elements as required for a specified accuracy [12]. The Onsager equations, also accounting for interface transfer, continue to be valid. The present manuscript has examined transport of two independent species (H and O). This resulted in two Nernst potentials and three parallel circuit elements (including one for electronic path) for any given segment (three segments—two interfacial and one bulk) in the equivalent circuit. The generalization of this result is that if there are  $N$  independent transporting ionic species, there will be  $N$  Nernst potentials and  $(N + 1)$  parallel circuit elements for any given segment.

### Acknowledgement

This work was supported by the U.S. Department of Energy under Grant Number DE-FG02-06ER46086.

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