

Transport mechanisms and voltage losses in PEMFC membranes and at electrodes: A discussion of open-circuit irreversibility

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Abstract

The transport properties of the membrane and the related dissipative phenomena significantly affect the performance of polymeric electrolyte membrane fuel cells. In this work the transport mechanisms taking place inside the membrane and the interaction of these with the adjacent electrodes will be analysed in some detail to gain a better understanding and control of cell performance and particularly of open-circuit voltage losses, which can be anything up to 30% of the effective voltage of an operating cell, as such an understanding could lead to significant technological improvements.

Here we present an analytical and interpretative description to try to identify the irreversible electrode phenomena under open-circuit conditions in terms of a dissipative steady-state and related “parasitic currents”.

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1. Introduction

It is well known that ionic conduction in polymeric proton conductive materials such as Nafion[®] takes place under conditions which are significantly different from those occurring in an electrolytic solution [1–3].

- First of all, only the positive charges are able to move and to carry current, while the negative ones, being an integral part of the solid structure of the membrane, cannot move at all.
- Secondly, the water-drag phenomena associated with positive charge migration are more important, the flow ratio between protons and water molecules being about 2.3. Positive charges do not migrate as free protons, but as solvated species and each positive ion consists of one proton and two or three molecules of solvent.
- Thirdly, as a consequence of the water-drag phenomena, the overall water flux through the membrane consists of two or more contributions: one due to solvation (“drag” term), which is directly associated with proton migration and the electric

current, and another or others connected with non-uniform membrane hydration (“diffusive” term) or to the pressure gradient (“forced” term).

- Fourthly, water cannot simply be considered as an inert solvent; on the contrary, the hydration level of the membrane and the water fluxes affecting hydration are important variables on which the transport characteristics of the membrane such as conductivity, diffusivity and permeability strongly depend.
- Finally, an apparently different, but probably connected, and perhaps even more intriguing question regards the open-circuit voltage losses (OCVL) of a polymeric electrolyte membrane fuel cell (PEMFC). The observed open-circuit voltages are about 0.2 V less than the ones expected according to equilibrium conditions (Nernst equation). These OCVL are generally and vaguely attributed to “dissipative phenomena”, which, obviously, also have to act, and in particular, under open-circuit conditions. On the contrary, when an interpretation in terms of “parasitic currents” is invoked [9,10], little effort is really made to explain how these currents can occur and act in an open circuit.

The further decrease in the cell voltage under closed-circuit conditions is better understood: the related dissipative phenomena have been much more closely studied and clearly determined

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Nomenclature

| | |
|---------------|--|
| b | see (A.4) |
| C | concentration, referring to the aqueous phase (kmol m ⁻³) |
| C' | concentration, referring to the membrane (kmol m ⁻³) |
| d | a-dimensional diffusivity, see (9) |
| D | diffusivity (m ² s ⁻¹) |
| e | swelling parameter of the membrane |
| F | Faraday's constant (A s kmol ⁻¹) |
| I | specific current (A m ⁻²) |
| k | equilibrium coefficient, see (A.1) |
| n | a-dimensional flux, see (9) |
| N | number of moles (kmol) |
| N | flux, referring to the aqueous phase (kmol m ⁻² s ⁻¹) |
| N' | flux, referring to the membrane (kmol m ⁻² s ⁻¹) |
| P | absolute pressure (J m ⁻³) |
| R | gas constant (J kmol ⁻¹ K ⁻¹) |
| T | absolute temperature (K) |
| V | voltage (J A ⁻¹) |
| \mathcal{V} | volume (m ³) |
| z | spatial co-ordinate (m) |

Greek letters

| | |
|---------------|--|
| α | mean degree of solvation |
| β | transfer coefficient |
| ε | volumetric fraction of the aqueous phase |
| η | a-dimensional voltage, see (9) |
| φ | volumetric fraction, see (2) |
| λ | degree of hydration, see (2) |
| π | a-dimensional pressure, see (9) |
| ξ | a-dimensional co-ordinate, see (9) |

Subscripts

| | |
|-----------|----------------------|
| A | anion |
| c | diffusive |
| i | generic component |
| o | open circuit |
| r | reference |
| t | total water |
| w | water |
| 2 | bisolvated proton |
| 3 | trisolvated proton |
| α | solvated proton mean |
| η | electrical |
| λ | hydration |
| π | pressure |

problem of the membrane resistance will be discussed in some detail, in particular from a rather fundamental point of view. For instance, the explicit consideration of the migration of the solvated molecules (H₂O)₂H⁺ and (H₂O)₃H⁺ could throw more light on the transport properties of the membrane and the related dissipative phenomena. In brief, it is hoped that any clarification of the transport mechanisms taking place inside the membrane and their interactions with the adjacent electrodes will be useful for understanding and, then, controlling the performance of PEMFCs as they become increasingly commercialised. In particular, any path towards understanding OCVL, which can be anything up to 30% of the effective voltage of an operating cell, can be an important premise for significant technological improvements.

2. Mass and charge transfer through the membrane

The membrane is considered here as a one-dimensional heterogeneous system made of a solid and an aqueous phase. The z co-ordinate is oriented through the membrane thickness from the anode ($z=0$) to the cathode ($z=s$). In the aqueous phase, the following components are considered:

- water H₂O (index w);
- the fixed negative ions (index A);
- the bisolvated proton (H₂O)₂H⁺ (index 2);
- the trisolvated proton (H₂O)₃H⁺ (index 3);
- as an alternative to the last two components, the mean solvated proton (H₂O) _{α} H⁺ (index α).

On the contrary, free H⁺ protons, mono-solvated (H₂O)H⁺ protons and multi-solvated protons are considered less important and are neglected. The dissolved neutral components such as H₂ and O₂ are similarly neglected initially because of their very low solubility.

The concentrations C_α (or C_2, C_3), C_w, C_A refer to the unit volume of the aqueous phase inside the pores of the membrane, while the total equivalent concentration of this aqueous phase, C_w , can be considered approximately constant and corresponding to the inverse of the molar volume of liquid water ($C_w \approx 1/18 \text{ mol cm}^{-3}$). In such a way swelling can be assumed to be proportional to the total hydration of the membrane.

$$\Delta\mathcal{V} = \frac{n_{wt}}{C_{wt}} \quad C_i = \frac{\mathcal{N}_i}{\Delta\mathcal{V}} = \frac{\mathcal{N}_i C_{wt}}{n_{wt}} \quad (1)$$

In a simplified description only the mean of the solvated protons and the solvation equilibrium mean constant (for instance $\alpha = 2.3 = \text{const.}$) can be considered under isothermal conditions. This simplification is discussed in [Appendix A](#).

In terms of the dimensionless variable

$$\varphi_\alpha = \frac{C_\alpha}{C_{wt}} \quad \varphi_w = \frac{C_w}{C_{wt}} \quad \lambda = \frac{n_{wt}}{n_A} = \frac{C_{wt}}{C_A} \quad (2)$$

the local electroneutrality condition and the local hydration of the membrane can be written as

$$C_\alpha = C_A \quad \varphi_\alpha = \frac{1}{\lambda} \quad d\varphi_\alpha = -\frac{d\lambda}{\lambda^2} \quad (3)$$

in terms of concentration polarisation, activation polarisation and electrical resistances of the membrane. Further considerations on the mass transfer inside the gaseous phases, which is responsible for the concentration polarisations and current limitations, will be specifically discussed elsewhere [4,5]. Here the

$$\alpha C_\alpha + C_w = C_{wt} \quad \alpha\varphi_\alpha + \varphi_w = 1 \quad d\varphi_w = \frac{\alpha}{\lambda^2} d\lambda \quad (4)$$

where α , φ_α , e , φ_w can be substantially assimilated to the volumetric fractions of the hydrated protons and water, respectively.

The fluxes passing through the membrane depend on the following driving forces:

- concentration gradients inside the aqueous phase, which induce diffusive component fluxes;
- voltage gradients, which induce the migration of the positive ions, but are also unbalanced global forces acting on the aqueous phase;
- pressure gradients, which act on the entire fluid;
- hydration gradients, which are connected to capillary forces and are then identifiable with an additional pressure gradient acting on the entire fluid.

By introducing an appropriate “diffusivity” for each driving force, the fluxes of the components (water and solvated protons) can be expressed as

$$N_\alpha = -D_{\alpha c} \frac{dC_\alpha}{dz} - D_{\alpha\eta} C_\alpha \frac{d(VF/RT)}{dz} - \left(\frac{D_{\alpha\pi} C_\alpha}{C_{wt} RT} \right) \frac{dP}{dz} - (D_{\alpha\lambda} C_\alpha) \frac{d\lambda}{dz} \quad (5)$$

$$N_w = -D_{wc} \frac{dC_w}{dz} - \left(\frac{D_{w\pi} C_w}{C_{wt} RT} \right) \frac{dP}{dz} - (D_{w\lambda} C_w) \frac{d\lambda}{dz} \quad (6)$$

so that the total water flux

$$N_{wt} = \alpha N_\alpha + N_w = -D_\eta C_\alpha \frac{d(VF/RT)}{dz} - \frac{D_\pi}{RT} \frac{dP}{dz} + D_\lambda C_{wt} \frac{d\lambda}{dz}, \quad (7)$$

which is a combination of the preceding ones, is also consistent with the momentum balance in the z direction. In fact, the aqueous phase undergoes pressure forces, capillary pressure forces and electrical forces acting on the protons, while the electrical forces on the anions are directly transferred to the solid support. The diffusive forces balance themselves so that the sum of the diffusive fluxes is zero. The other forces are balanced by shear stresses under a laminar (or, better, a viscous) regime, so that they can be assumed to be proportional to the velocity and the total water flux N_{wt} , as in Eq. (7).

Moreover, as Eq. (7) is a linear combination of Eqs. (5) and (6), the following conditions hold:

$$D_{\alpha c} = D_{wc} = D_c \quad D_\pi = \frac{\alpha D_{\alpha\pi} C_\alpha + D_{w\pi} C_w}{C_{wt}} \quad (8)$$

$$D_\eta = \alpha D_{\alpha\eta} \quad D_\lambda = \frac{\alpha D_{\alpha\lambda} C_\alpha + D_{w\lambda} C_w}{C_{wt}}$$

By introducing the dimensionless variables and parameters defined in the equations in (2) and in the following:

$$n_i = \frac{N_i s}{C_{wt} D_w} \quad d_i = \frac{D_i}{D_c} \quad (9)$$

$$\eta = \frac{VF}{RT} \quad \pi = \frac{P}{C_{wt} RT} \quad \xi = \frac{z}{s}$$

Eqs. (5)–(7) can be written

$$n_\alpha = - \left(d_{\alpha\lambda} \varphi_\alpha - \frac{1}{\lambda^2} \right) \frac{d\lambda}{d\xi} - (d_{\alpha\eta} \varphi_\alpha) \frac{d\eta}{d\xi} - (d_{\alpha\pi} \varphi_\alpha) \frac{d\pi}{d\xi}$$

$$= - \left(d_{\alpha\lambda} - \frac{1}{\lambda^2} \right) \frac{d\lambda}{d\xi} - \left(\frac{d_\eta}{\alpha\lambda} \right) \frac{d\eta}{d\xi} - \left(\frac{d_{\alpha\pi}}{\lambda} \right) \frac{d\pi}{d\xi} \quad (10)$$

$$n_w = - \left(d_{w\lambda} \varphi_w + \frac{\alpha}{\lambda^2} \right) \frac{d\lambda}{d\xi} - (d_{w\pi} \varphi_w) \frac{d\pi}{d\xi}$$

$$= - \left(d_\lambda - \frac{\alpha d_{\alpha\lambda}}{\lambda} + \frac{\alpha}{\lambda^2} \right) \frac{d\lambda}{d\xi} - \left(1 - \frac{\alpha d_{\alpha\pi}}{\lambda} \right) \frac{d\pi}{d\xi} \quad (11)$$

$$n_{wt} = \alpha n_\alpha + n_w = -d_\lambda \frac{d\lambda}{d\xi} - \left(\frac{d_\eta}{\lambda} \right) \frac{d\eta}{d\xi} - d_\pi \frac{d\pi}{d\xi} \quad (12)$$

$$\alpha d_{\alpha\pi} \varphi_\alpha + d_{w\pi} \varphi_w = d_\pi \quad \alpha d_{\alpha\lambda} \varphi_\alpha + d_{w\lambda} \varphi_w = d_\lambda$$

$$d_{\alpha\eta} = \frac{d_\eta}{\alpha} \quad (13)$$

Some further comments are useful. The description (5)–(8) (or (10)–(13) in dimensionless form) of the mass and charge fluxes passing through a PEMFC membrane is somewhat more detailed and more consistent than the one presented and used in our previous works [6–8]. The present description must be considered, first of all, as a research tool, while the previous is more suitable, given the actual state of our knowledge, for applicative uses, for instance in simulation. In Appendix B, however, it will be shown that Eqs. (5)–(8) are coherent with the previous description and can be reduced to it.

In particular, the fluxes mentioned here refer to the unit area of the aqueous phase, so that some further mathematical steps are necessary in order to obtain fluxes per unit area of the membrane (see Appendix B). An analysis of the problem in terms of the transport properties of the aqueous phase has been preferred, because this can be considered, to some extent, independent of the degree of hydration of the membrane. On the other hand, the hydration λ must be explicitly considered in the capillary forces and directly affects the molar fractions φ_α (or volumetric fractions $\alpha\varphi_\alpha$) of the solvated protons.

The consideration of a unique proton species with a constant, mean, solvation number α would seem to be an over simplification. As a matter of fact (see Appendix A), this choice is completely correct only when a thermodynamic equilibrium condition acts on the proton species locally.

The generalised Nernst–Planck expression, according to which the phenomenological coefficients of the electrical, diffusive and pressure forces have been determined, could also be too simple. For this reason, it is worth noting that other conditions

acting on the various mobility coefficients, such as those below, could be introduced:

$$d_\eta = d_\pi = 1 \quad d_\lambda \neq 1 \quad (14)$$

Roughly speaking, the electrical forces per unit volume are $C_\alpha d(VF)/dz$ and the corresponding pressure forces are dP/dz , while the capillarity forces are only proportional to $RT d\lambda/dz$. Therefore, D_η and D_π could be assumed to be equal, while D_λ is certainly independent. As the diffusive forces of an ideal system are $RT dC_w/dz$, D_c could also be assimilated, at least as a first approximation, to D_η and D_π , as is suggested by the ideal form of the Nernst–Planck law. Nevertheless, to avoid oversimplifications, the following discussion will be developed without taking into account the first of the equations in (14), which will only occasionally be referred to and discussed in terms of orders of magnitude.

3. Open-circuit membrane

In the system (10)–(13) the hydration, pressure and voltage gradients are usually considered as independent variables on which the fluxes depend. On the contrary, the fluxes can also be treated as independent variables in order to determine what gradients are consistent with a given set of fluxes. In particular, beside the equilibrium condition of the membrane, in which all fluxes as well as all gradients vanish and the membrane voltage ought to obey the Nernst law, stationary conditions, in which only one or some fluxes are zero, are also possible.

A simple but particularly interesting condition is that of the open-circuit ($n_\alpha = 0$), in which Eqs. (10)–(13) become

$$\frac{d\eta}{d\xi} = -\frac{[(\alpha d_{\alpha\lambda} - \alpha/\lambda)(d\lambda/d\xi) + (\alpha d_{\alpha\pi})d\pi/d\xi]}{d_\eta}, \quad n_\alpha = 0 \quad (15)$$

$$n_{wt} = n_w = -\left(d_\lambda - \frac{\alpha d_{\alpha\lambda}}{\lambda} + \frac{\alpha}{\lambda^2}\right) \frac{d\lambda}{d\xi} - \left(1 - \frac{\alpha d_{\alpha\pi}}{\lambda}\right) \frac{d\pi}{d\xi}, \quad n_\alpha = 0 \quad (16)$$

The open-circuit condition does not necessarily correspond to null gradients, but only imposes a relationship on the gradients and the total water flux. In other words, if the membrane is subjected to external driving forces in terms of hydration and/or pressure gradients, some related voltage gradients could also subsist under open-circuit conditions. Pressure forces, as well as capillary forces induce a water flux and, then, tend to induce a proton-drag flux; as the latter is not possible because of the open-circuit constraint, an antagonist voltage gradient has to occur as well.

The condition requiring that *all* gradients are zero (hydration, voltage, pressure, temperature), and not that requiring only that the current is zero, is to be considered sufficient for thermodynamic equilibrium throughout the membrane. The null-current (open-circuit) condition is only necessary for the equilibrium and it is consistent with a dissipative steady-state (or a dissipative structure), according to Prigogine's terminology [11].

In brief, the immobilisation of the charges under the open-circuit condition can co-exist with a water flux through the membrane and a corresponding over potential. For instance, under open-circuit and isobar conditions, Eq. (16)

$$\frac{d\eta}{d\xi} = n_{wt} \frac{[(\alpha d_{\alpha\lambda} - \alpha/\lambda)/(d_\lambda - \alpha d_{\alpha\lambda}/\lambda + \alpha/\lambda^2)]}{d_\eta}, \quad n_\alpha = 0; \quad \frac{d\pi}{d\xi} = 0; \quad \frac{d\eta}{d\xi} < 0 \quad (17)$$

indicates that a voltage loss through the membrane may be associated with a negative water flux (that is from the cathode to the anode).

As the membrane is to some extent also permeable to molecular hydrogen, a slight positive hydrogen flux (from the anode to the cathode) can be assumed; this flux should undergo oxidation at the cathode with the formation of water and should so induce a counter-flux of water and an open-circuit voltage loss.

At this point the question is whether this phenomenon is truly important or not; here the discussion can only be initiated. In the first place, the quantity of open-circuit water flux that could cause the observed voltage losses depends on the values of the mobility coefficients. By allowing for the second equation in (13) and the assumptions $\lambda \gg \alpha > 1$, $d_{\alpha\lambda}$, $d_{\alpha\pi}$ of the order of unity or greater, Eq. (17) can be written

$$(n_{wt})_o = \left(\frac{d\eta}{d\xi}\right)_o \frac{d_\eta}{\lambda} \frac{[(\lambda^2/\alpha)d_{w\lambda} - \lambda d_{w\lambda} + 1]}{\lambda d_{\alpha\lambda} - 1} \approx \left(\frac{d\eta}{d\xi}\right)_o \frac{d_\eta}{\alpha} \frac{d_{w\lambda}}{d_{\alpha\lambda}} \quad (18)$$

Then, a comparison with a reference condition related to the usual running of the cell under uniform pressure and hydration

$$(n_\alpha)_r \approx -\left(\frac{d\eta}{d\xi}\right)_r \frac{d_\eta}{\lambda} \quad (19)$$

yields

$$\frac{(n_{wt})_o}{(n_\alpha)_r} \approx -\frac{\lambda}{\alpha} \frac{(d\eta/d\xi)_o}{(d\eta/d\xi)_r} \frac{d_{w\lambda}}{d_{\alpha\lambda}} \approx -3 \left(\frac{d_{w\lambda}}{d_{\alpha\lambda}}\right) \quad (20)$$

By assuming that $(d\eta/d\xi)_r$ is about three times greater than $(d\eta/d\xi)_o$ ($\Delta V_o \approx 0.2$ V; $\Delta V_r \approx 0.6$ V) and $\lambda/\alpha \approx 9$, Eq. (20) demonstrates that the open-circuit water flux responsible for the observed voltage losses is very low ($|(n_{wt})_o/(n_\alpha)_r| \ll 1$) only for $d_{w\lambda}/d_{\alpha\lambda} \ll 1$. On the contrary, if $d_{w\lambda}/d_{\alpha\lambda} \approx 1$, Eq. (14) demonstrates that the open-circuit water flux and the corresponding hydrogen consumption should be high enough to be evident.

Similar considerations can be made directly from Eq. (17). The mobility coefficient of the protons in relation to the hydration gradients ($d_{\alpha\lambda}$) could differ greatly from $d_{w\lambda}$, so that the denominator of the second term in (17) could be very low and the voltage loss could become sensitive to the water flux. In this case open-circuit voltage losses of the order of the observed ones could be foreseen in association with molecular hydrogen and water fluxes that are substantially low enough to pass unnoticed.

The existence of transport properties of the charged species inside the membrane system very different to those of the neutral ones is not unlikely. A hydration gradient is associated with the

spatial asymmetry of the porous system through the membrane thickness (for instance the pore diameter will increase with the degree of hydration), so that asymmetry in the geometric disposition of the negative charges fixed on the pore surface could also occur. The electrical forces arising from this asymmetrical arrangement are likely to be much greater than the capillarity forces, so that the additional electrical forces due to hydration gradients acting on protons (that is the principal contribution to $d_{\alpha\lambda}$) could be much greater than the capillary pressure forces acting on neutral water (that is $d_{w\lambda}$).

Secondly, at first sight, the direct consideration of the extent of the hydrogen fluxes also indicates that this flux is rather unlikely to be the only one responsible for the relevant OCVL, unless Eq. (14) is not true at all. An estimation of the order of magnitude of the flux of the molecular hydrogen through the membrane and the corresponding counter-flux of water is presented in the following section. The hydrogen flux is very low, depending on its solubility in the membrane system. If this is assimilated to its solubility in water, Eq. (14) is assumed to hold and the reference values $\alpha = 2.3$ and $\lambda = 20$ are used. Eq. (17) foresees voltage losses much lower than 0.2 V. However, besides the question of the correctness of Eq. (14), hydrogen solubility could also be strongly affected by adsorption phenomena or, at least, by the strong non-ideality of the aqueous phase inside the membrane, so that much greater hydrogen fluxes could be possible.

In our opinion the question of hydrogen solubility, as well as that related to the asymmetry effects of the hydration, are worth further theoretical and experimental attention, as they could lead to a better determination of at least a part of the open-circuit irreversibility.

4. Membrane stability

When discussing fluxes which cross the membrane under open-circuit conditions, another set of questions appears to be of some interest and not completely marginal or fanciful. These questions involve membrane stability and the origin of the driving forces that act on the membrane. One could ask oneself, in particular, whether the absence of gradients imposed by external constraints is equivalent to that of null gradients and is, therefore, a sufficient condition for equilibrium or, on the contrary, the spontaneous creation of gradients inside the membrane is possible as a result of local instability, perhaps in connection with apparently secondary phenomena. For instance, when recalling that the charge vectors are at least two (bi- and trisolvated protons), the open-circuit condition appears to be compatible with fluxes in the opposite direction to the two vectors, so that the problem of the stability of the equilibrium becomes more subjective and delicate.

Quantitative checks of thermal fluxes (both conductive and enthalpic), indicate that heat transfer through the membrane is very likely to be stable, which means that the total equivalent conductivity of the membrane system is positive. Similar results can be obtained, at least at the first approach, when the water transfer is considered, that is the total equivalent diffusivity of the water is positive too. Nevertheless, it remains difficult to definitely exclude the existence of any sensitivity or instabil-

ity phenomenon able to amplify the effects of the unbalancing of other, non-electrical, driving forces in terms of appreciable voltage differences. The concentration gradients of molecular hydrogen (or oxygen) and the affinity of the oxidation reaction are examples of these kinds of forces.

An example of a possible source of instability can be given as follows. In Eq. (20), the electrical forces associated with hydration gradients, besides having a greater absolute value than the capillary ones, could even have the opposite sign, that is $|d_{w\lambda}/d_{\alpha\lambda}| \ll 1$ with $d_{w\lambda} < 0$. In such a case, the water flux associated with a voltage loss should go from the anode to the cathode and could be related to the occurrence of instability phenomena. In other words, if

$$d_{\lambda} = \alpha d_{\alpha\lambda} \varphi_{\alpha} + d_{w\lambda} \varphi_w \approx \alpha \frac{d_{\alpha\lambda}}{\lambda} < 0 \quad (21)$$

the total water flux should tend to go towards the increasing humidity, due to the drag effect of the solvated molecules, and should so create a spontaneous increment in the hydration gradient.

5. Fluxes of neutral hydrogen

In the last section we have possibly tended to speculate too much. To return to more concrete arguments, it seems to be useful to evaluate the order of magnitude of the fluxes of the neutral reagents, hydrogen and oxygen, which cross a PEMFC membrane and cause

- the consumption of reagents without a corresponding production of energy;
- voltage losses that penalise the conversion efficiency of the overall electrochemical reaction.

These voltage losses, which also exist in an open circuit [9,10], can be

- in part closely associated with the fluxes of the inert gas and then be localised inside the membrane;
- in part the result of the interaction of inert fluxes with an electrode reaction, and so localised only at the electrode.

In the following, the solubility of molecular hydrogen and oxygen in water will be used; the correctness of all the considerations made depends on the accuracy of such data in representing the solubility of the membrane system. The solubility of hydrogen in water at temperatures similar to those occurring in a cell is very low. Henry's constants for hydrogen and oxygen at 100 °C are, respectively, 7.45×10^4 and 7.01×10^4 atm. At an atmospheric PEMFC anode, reference can be made to about 1 atm of hydrogen, with an equilibrium molar fraction of about 1.3×10^{-5} , while at the cathode the oxygen partial pressure is of the order of 0.2 atm or lower, with an equilibrium molar fraction lower than 2.8×10^{-6} . Even allowing for the stoichiometry of the oxidation reaction, hydrogen exceeds oxygen and it is therefore reasonable to make reference to a molecular hydrogen flux which dissolves at the anode, migrates through the water phase

inside the membrane and ends up reacting with the oxygen at (or near) the cathode, so producing water. This water can counter-diffuse towards the anode and cause a (little ?) voltage loss in the membrane.

Due to its very low solubility, this molecular hydrogen flux must, in turn, be very low. Making reference to an effective diffusivity of the membrane of $10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and a membrane thickness of 0.1 cm a hydrogen flux N'_{H_2} of the order of $7 \times 10^{-12} \text{ mol cm}^{-2} \text{ s}^{-1}$ is obtained, which corresponds to a current of the order of $1.4 \times 10^{-6} \text{ A cm}^{-2}$.

The insignificance of these neutral hydrogen fluxes in a closed circuit should make it possible to ignore their cross-effects on the other, much more important fluxes of water and protons. On the other hand, the persistence of such irreversible phenomena in an open circuit makes it necessary to investigate the matter further.

As already said in the previous section, hydrogen fluxes of such an order of magnitude could induce significant voltage losses through the membrane only in association with important asymmetries in the conductivity coefficients and the pore geometry. It still remains to consider what happens outside the membrane and, in particular, what effects could be induced on the cathode, by a hydrogen flux and its consequent oxidation reaction.

6. Open-circuit electrode

The fact that such low fluxes cause such significant irreversibility effects suggests that further study should also, or prevalently, be oriented towards strongly non-linear and sensitive phenomena, such as the activation mechanisms on the electrodes.

The neutral oxygen and hydrogen fluxes that enter the cathode and undergo an oxidation reaction there correspond to a parasitic current completely inside the cathode. Then, in a closed circuit, the net current can be considered as the difference between the total current I_t and the parasitic current I_{oc}

$$I = I_t - I_{oc} = I_o \{ \exp[\beta(\eta + \eta_o)] - \exp[-(\beta - 1)(\eta + \eta_o)] \} - I_o \{ \exp[\beta\eta_o] - \exp[-(\beta - 1)\eta_o] \} \quad (22)$$

The parasitic current is, in turn, connected to a voltage loss η_o , which also exists in an open circuit, when the net current vanishes, together with the additional voltage loss η :

$$I_{oc} = I_o \{ \exp[\beta\eta_o] - \exp[-(\beta - 1)\eta_o] \} \quad (23)$$

By assuming $\beta=0.5$ and $\eta_o \approx 12$, that is an OCV voltage loss of about 0.2 V, the preceding equations can be reduced to the Tafel form

$$I_{oc} = I_o \exp(\beta\eta_o) \quad (24)$$

$$I = I_o \exp(\beta\eta_o) [\exp(\beta\eta) - 1] = I_o \exp(\beta\eta_o) \exp(\beta\eta) = I_{oc} \exp(\beta\eta) \quad (25)$$

By making reference to the aforesaid indicative value of the molecular hydrogen flux and the corresponding parasitic

current $I_{oc} = 1.4 \times 10^{-6} \text{ A cm}^{-2}$, an exchange current value $I_o = 3.5 \times 10^{-9} \text{ A cm}^{-2}$ should be obtained. Therefore, a typical PEMFC cathode could be described in one of the following ways.

- (a) The cathode is characterised by an exchange current

$$I_o^* = I_{oc} = 1.4 \times 10^{-6} \text{ A cm}^{-2}$$

and an open-circuit voltage loss

$$\eta_o = 0.2 \text{ V}$$

which is attributed to imprecisely-stated dissipative phenomena. Further voltage losses under closed-circuit conditions follow Tafel's law:

$$\eta = \ln \left(\frac{I}{I_o^*} \right).$$

- (b) The cathode is characterised by a much lower exchange current

$$I_o = 3.5 \times 10^{-9} \text{ A cm}^{-2}$$

and a molecular hydrogen flux corresponding to a very low parasitic current

$$I_{oc} = 1.4 \times 10^{-6} \text{ A cm}^{-2}$$

with which a voltage loss of

$$\eta_o = 0.2 \text{ V}$$

is associated. The total open-circuit voltage losses follow Tafel's law:

$$\eta + \eta_o = \ln \left(\frac{I}{I_o} \right) \quad \text{with} \quad \eta = \ln \left(\frac{I}{I_{oc}} \right) \quad \text{and}$$

$$\eta_o = \ln \left(\frac{I_{oc}}{I_o} \right).$$

The two descriptions are identical and differ only in the terms used, which seem to be more analytical and interpretative in the second, in which the possibility of identifying the irreversible electrode phenomena under open-circuit conditions in terms of a "parasitic current" is proposed.

The important point is that this parasitic current is here associated with a hydrogen flux that crosses the membrane, under steady-state, non-equilibrium, open-circuit conditions. On the other hand, only more accurate experimental investigations, aimed at measuring small open-circuit hydrogen fluxes and internal currents would make it possible to verify or refute this interpretation. While we are waiting for more concrete proof, the use of the term "parasitic current" to explain the open-circuit voltage losses, or a part of them, remains as vague as the apparently more generic "dissipative phenomena".

7. Conclusions

The performance of polymeric electrolyte membrane fuel cells strongly depends on transport mechanisms and dissipative phenomena that occur inside the membrane and the electrodes. This work could represent an interpretative contribution to understanding open-circuit voltage losses, which can be up to 30% of the effective voltage of an operating cell and cause considerable damage from a technological point of view.

In particular, the transport mechanisms taking place inside the membrane and the interaction of these with the adjacent electrodes have been analysed in detail to better understand and control cell performance.

In an open circuit, low hydrogen fluxes could be associated with strongly non-linear and sensitive phenomena, such as the activation mechanisms on the electrodes. An analytical and interpretative description has been proposed to try to identify the irreversible electrode phenomena under open-circuit conditions in terms of parasitic currents.

Therefore, we assume that parasitic currents are linked to a hydrogen flux which would cross the membrane, under steady-state, non-equilibrium, open-circuit conditions: only very accurate experimental investigations aimed at measuring small open-circuit hydrogen fluxes and internal currents would make it possible to verify the interpretation proposed in this work.

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Appendix A

If the bihydrated and trihydrated protons are considered separately and the ratio of their respective concentrations is assumed to obey an equilibrium relationship of the type

$$C_3 = k(\lambda)C_2 \quad (\text{A.1})$$

instead of that in Eqs. (3) and (4), the following are obtained:

$$\varphi_2 + \varphi_3 = \varphi_2(1 + k) = \frac{1}{\lambda} \quad d\varphi_2 = -b \frac{d\lambda}{\lambda^2}$$

$$d\varphi_3 = -(1 - b) \frac{d\lambda}{\lambda^2} \quad (\text{A.2})$$

$$2\varphi_2 + 3\varphi_3 + \varphi_w = \varphi_2(2 + 3k) + \varphi_w = 1$$

$$d\varphi_w = (3 - b) \frac{d\lambda}{\lambda^2} \quad (\text{A.3})$$

where

$$b = \frac{1 + k + \lambda dk/d\lambda}{(1 + k)^2} \quad (\text{A.4})$$

and the definition of the mean degree of hydration (or solvation) of the protons can be stated as

$$\alpha = \frac{2\varphi_2 + 3\varphi_3}{\varphi_2 + \varphi_3} = \frac{2 + 3k}{1 + k} \quad (\text{A.5})$$

In particular, Eq. (A.5) underlines that the mean solvation degree α , which depends on the equilibrium constant k , can be considered here as a function of the local hydration of the membrane λ , which is restricted, by the particular assumption made about the possible proton species, to a range of values between 2 and 3.

The fluxes of the three species considered are now

$$N_2 = -D_{2c} \frac{dC_2}{dz} - D_{2\eta} C_2 \frac{d(VF/RT)}{dz} - \left(\frac{D_{2\pi} C_2}{C_{wt} RT} \right) \frac{dP}{dz} - (D_{2\lambda} C_2) \frac{d\lambda}{dz} \quad (\text{A.6})$$

$$N_3 = -D_{3c} \frac{dC_3}{dz} - D_{3\eta} C_3 \frac{d(VF/RT)}{dz} - \left(\frac{D_{3\pi} C_3}{C_{wt} RT} \right) \frac{dP}{dz} - (D_{3\lambda} C_3) \frac{d\lambda}{dz} \quad (\text{A.7})$$

$$N_w = -D_{wc} \frac{dC_w}{dz} - \left(\frac{D_{w\pi} C_w}{C_{wt} RT} \right) \frac{dP}{dz} - (D_{w\lambda} C_w) \frac{d\lambda}{dz} \quad (\text{A.8})$$

or, in dimensionless terms,

$$n_2 = - \left(d_{2\lambda} \varphi_2 - d_{2c} \frac{b}{\lambda^2} \right) \frac{d\lambda}{d\xi} - (d_{2\eta} \varphi_2) \frac{d\eta}{d\xi} - (d_{2\pi} \varphi_2) \frac{d\pi}{d\xi} \quad (\text{A.9})$$

$$n_3 = - \left[d_{3\lambda} k \varphi_2 - d_{3c} \frac{1 - b}{\lambda^2} \right] \frac{d\lambda}{d\xi} - (d_{3\eta} k \varphi_2) \frac{d\eta}{d\xi} - (d_{3\pi} k \varphi_2) \frac{d\pi}{d\xi} \quad (\text{A.10})$$

$$n_w = - \left[d_{w\lambda} \varphi_w + d_{wc} \frac{3 - b}{\lambda^2} \right] \frac{d\lambda}{d\xi} - (d_{w\pi} \varphi_w) \frac{d\pi}{d\xi} \quad (\text{A.11})$$

Obviously, by adding Eqs. (A.9) and (A.10), Eq. (10) is once again

$$n_\alpha = - \left(\frac{d_{\alpha\lambda}}{\lambda} - \frac{1}{\lambda^2} \right) \frac{d\lambda}{d\xi} - \left(\frac{d_{\alpha\eta}}{\lambda} \right) \frac{d\eta}{d\xi} - \left(\frac{d_{\alpha\pi}}{\lambda} \right) \frac{d\pi}{d\xi} \quad (10')$$

under the conditions

$$bd_{2c} + (1 - b)d_{3c} = 1 \quad d_{2\lambda} + kd_{3\lambda} = (1 + k)d_{\alpha\lambda} \quad (\text{A.12})$$

$$d_{2\eta} + kd_{3\eta} = (1 + k)d_{\alpha\eta} \quad d_{2\pi} + kd_{3\pi} = (1 + k)d_{\alpha\pi}$$

Similarly, by combining Eqs. (A.9)–(A.11) in the total water flux

$$n_{wt} = 2n_2 + 3n_3 + n_w \quad (\text{A.13})$$

Eq. (12) is once again

$$n_{wt} = \alpha n_\alpha + n_w = -d_\lambda \frac{d\lambda}{d\xi} - \frac{1}{\lambda} \frac{d\eta}{d\xi} - \frac{d\pi}{d\xi} \quad (12')$$

under the further conditions

$$2bd_{2c} + 3(1 - b)d_{3c} - (3 - b) = 0$$

$$\begin{aligned} 2d_{2\eta} + 3kd_{3\eta} &= (1 + k)d_{\eta} \\ 2d_{2\pi} + 3kd_{3\pi} - (2 + 3k)d_{w\pi} &= \lambda(d_{\pi} - d_{w\pi})(1 + k) \end{aligned} \quad (\text{A.14})$$

$$2d_{2\lambda} + 3kd_{3\lambda} - (2 + 3k)d_{w\lambda} = \lambda(d_{\lambda} - d_{w\lambda})(1 + k)$$

The conditions (A.12) and (A.14) show that, as long as the local equilibrium condition (A.1) holds, univocal links also hold among the mobilities of the proton species (for instance $d_{2\eta}$ and $d_{3\eta}$) and that of the mean solvated species (for instance d_{η}).

Appendix B

Eqs. (5) and (6) aim to describe mass and charge transport phenomena occurring in the aqueous phase of a heterogeneous membrane system. The fluxes and the concentrations refer to the aqueous phase, so that N_i is moles of i per unit of aqueous-phase area and C_i is moles of i per unit of aqueous-phase volume. Moreover, in Eqs. (5) and (6) the gradients dC_i/dz (that is the diffusive forces) and $d\lambda/dz$ (that is the capillary forces) are considered separately. So, two steps have to be made in order to bring the present description back to the one used more pragmatically in our simulation works.

As a first step, by using Eqs. (2)–(4), the concentration gradients and the hydration gradients can be transformed into each other by the differential relationships

$$d\lambda = - \left(\frac{C_{wt}}{C_{\alpha}^2} \right) dC_{\alpha} = \left(\frac{C_{wt}}{\alpha C_{\alpha}^2} \right) dC_w \quad (\text{B.1})$$

So, by using the equations in (B.1), Eqs. (5) and (6) can be written

$$\begin{aligned} N_{\alpha} &= - \left[D_{\alpha c} - \left(D_{\alpha \lambda} \frac{C_{wt}}{C_{\alpha}} \right) \right] \frac{dC_{\alpha}}{dz} - \left(D_{\alpha \eta} C_{\alpha} \frac{F}{RT} \right) \frac{dV}{dz} \\ &\quad - \left(D_{\alpha \pi} \frac{C_{\alpha}}{C_{wt} RT} \right) \frac{dP}{dz} \end{aligned} \quad (\text{B.2})$$

$$N_w = - \left[D_{wc} + \left(D_{w\lambda} C_w \frac{C_{wt}}{\alpha C_{\alpha}^2} \right) \right] \frac{dC_w}{dz} - \left(\frac{D_{w\pi} C_w}{C_{wt} RT} \right) \frac{dP}{dz} \quad (\text{B.3})$$

In the second step the fluxes N_i and the concentrations C_i have to be transformed into the fluxes N'_i and the concentrations C'_i , which refer to the whole heterogeneous membrane system

$$N_i \varepsilon = N'_i \quad C_i \varepsilon = C'_i \quad (\text{B.4})$$

by using the volumetric fraction ε of the aqueous phase in relationship to the volume of the membrane system. This volumetric

fraction is directly linked to (and roughly coincides with) the swelling parameter e

$$\varepsilon = \frac{e}{1 + e} \quad (\text{B.5})$$

and can also be expressed in terms of the concentration C'_{α}

$$\varepsilon = \frac{1 - C'_{\alpha}}{C'_{\alpha s}} = \frac{1 - C'_{\alpha}}{C'_{As}} \quad (\text{B.6})$$

so that the following differential relationships between dC_i and dC'_i can be obtained:

$$dC'_{\alpha} = \varepsilon^2 dC_{\alpha} \quad dC'_w = \left[\varepsilon^2 + \lambda \varepsilon \frac{1 - \varepsilon}{\alpha} \right] dC_w \quad (\text{B.7})$$

By substituting Eqs. (B.4) and (B.7) in (B.2) and (B.3) and recalling (2)–(4), the final form

$$\begin{aligned} N'_{\alpha} &= - \left[\frac{D_{\alpha c} - \lambda D_{\alpha \lambda}}{\varepsilon} \right] \frac{dC'_{\alpha}}{dz} - \left(D_{\alpha \eta} C_{wt} \varepsilon \frac{F}{\lambda RT} \right) \frac{dV}{dz} \\ &\quad - \left(\frac{D_{\alpha \pi} \varepsilon}{\lambda RT} \right) \frac{dP}{dz} \end{aligned} \quad (\text{B.8})$$

$$N'_w = - \left[\frac{\alpha D_{wc} + D_{w\lambda}(\lambda - \alpha)\lambda}{\lambda - (\lambda - \alpha)\varepsilon} \right] \frac{dC'_w}{dz} - \left[\frac{D_{w\pi}(\lambda - \alpha)\varepsilon}{\lambda RT} \right] \frac{dP}{dz} \quad (\text{B.9})$$

of the flux equations is obtained, which has the same structure as Eqs. (10) and (11) of the reference [6] and can easily be compared to them. The transformation of one set of diffusivity coefficients into the other is now quite straightforward.

References

- [1] J.O'M. Bockris, D.M. Dražić, *Electro-Chemical Science*, Taylor & Francis, London, 1972.
- [2] F. Hine, *Electrode Processes and Electrochemical Engineering*, Plenum Press, New York, 1985.
- [3] J. Newman, *Electrochemical Systems*, Prentice-Hall, Englewood Cliffs, NJ, 1973.
- [4] E. Arato, P. Costa, *J. Power Sources* 158 (2006) 200–205.
- [5] E. Arato, M. Pinna, P. Costa, *J. Power Sources*, in press.
- [6] M. De Francesco, E. Arato, P. Costa, *J. Power Sources* 132 (2004) 127.
- [7] A. Serrafiero, E. Arato, P. Costa, Proc. H2-AGE: When, Where, Why (H2www, Pisa, Italy, May 2004) in *Chemical Engineering Transactions*, 4 (2004) 423 (Edit. Sauro Pierucci, AIDIC Servizi S.r.l., Milano).
- [8] A. Serrafiero, E. Arato, P. Costa, *J. Power Sources* 145 (2005) 470.
- [9] Y.W. Rho, S. Srinivasan, Y.T. Kho, *J. Electrochem. Soc.* 141 (1994) 2089.
- [10] P. Costamagna, S. Srinivasan, *J. Power Sources* 102 (2001) 242.
- [11] P. Glandsdorff, I. Prigogine, *Thermodynamic Theory of Structure, Stability and Fluctuations*, Wiley, London, 1971.