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Thermodynamically consistent electro-chemo-mechanical model for polymer membranes

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ABSTRACT

Nafion membranes, are polymeric thin films widely employed in micro-batteries and fuel cells. These devices are expected to play a key role in the next generation energy systems for use in vehicles as a replacement to combustion engines. In fact, a minimum environmental impact is guaranteed by reduced carbon dioxide emissions. It is usually complicated to investigate the behavior of thin membranes through experiments. Therefore, numerical simulations are carried out in order to enable a better understanding of the phenomena and of the multi-field couplings occurring in polymeric membranes.

A continuum-based, three-dimensional and electro-chemo-mechanical (ECM) model for a hydrated polymer membrane is presented. Different effects are taken into account: (i) mechanics, (ii) water uptake, (iii) ion transport, and (iv) electrostatics. The dissipation inequality drives the choice of the suitable constitutive equations of the multi-physics theory. In the mechanical field, an additive decomposition of the deformation gradient in (i) a distortion part, related to the ion motion, and (ii) an elastic part, is assumed. The multi-field model is numerically solved within the finite element framework. Time-dependent simulations are performed by using the commercial tool COMSOL Multiphysics. Furthermore, two closed form solutions are obtained by using (i) a one-dimensional reduced model and (ii) an approach based on the bar theory with an electro-chemical distortion field.

Keywords: Nafion, Thin Polymeric Membrane, Thermodynamically Based Theory, Multi-Field Model, Numerical Simulation, Finite Element Method

1. INTRODUCTION

Polymeric thin films, such as the Nafion membranes developed by DuPont Co., are widely employed in micro-batteries and proton-exchange-membrane fuel cells. These devices can guarantee an efficient and uncontaminated mechanism to convert energy from chemical to electrical preventing many global issues, such as (i) climate changes due to air pollution, (ii) ozone layer depletion and (iii) the dwindling world supplies of fossil fuels. Its electro-chemo-mechanical properties make Nafion membranes a promising candidate for new applications which are expected to play a key role in the next generation energy systems for use in vehicles as a replacement to combustion engines. The typical characteristics of Nafion-based technologies, such as (i) reduced carbon dioxide emissions, (ii) renewable sources and (iii) modern energy carriers, pave the way to a vast revolutionary change in the field of electricity.¹⁻³

Numerical simulations are useful tools in order to investigate the dependence of the electro-chemo-mechanical response of Nafion membranes on different working conditions, as well as to better understand the behavior of

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these devices and to further develop the current state-of-the-art of this technology. Typically, numerical simulations are based on the implementation of mathematical models which can generally be separated into (i) phenomenological models that fit the curves of experimental data, and (ii) physics-based models that attempt to predict the material response from governing equations.⁴ The purpose of this paper is to develop a continuum-based and physics-based model which starts from the balance equations of electrostatics, ions diffusion, and mechanics to derive a fully coupled formulation. A free energy is introduced in order to describe the thermodynamics of the system and to fulfill the requirements of consistency with the dissipation inequality.

As a first step, a linearized model is implemented. It is imagined that the Nafion membrane has a stress-free hydrated passive state and the electro-chemo-mechanical response of the membrane from this state is studied. It is worth noting that the hydrated state may also be very different from the reference dry state, that is, the deformation from the dry to the hydrated state may be finite. On the contrary, once the membrane is activated through the application of a (small) difference in voltage, deformations from the hydrated state to the active state are small and can be described within the context of a linearized mechanics. In particular, it is assumed that the mechanical response of the membrane changes under different hydration conditions, following laws which have been already proposed in Refs. 5,6, where a formal linearization procedure is performed.

Following the aim to identify the simplest way to study the electro-chemo-mechanical response of the Nafion membrane without neglecting relevant elements, the mathematical model has been implemented at different levels. A fully coupled three-dimensional model is implemented within a commercial finite element software and the outcomes of the simulations are compared with the ones obtained from the semi-analytical solution of an approximate one-dimensional model. Finally, an analogy with a bar model is also proposed.

2. ELECTRO-CHEMO-MECHANICAL MODEL

Polymeric films consist of a cross-linked network of bound ionic groups and a liquid phase with mobile ions. The solvent-ions-polymer mixture is treated as a single homogenized continuum body allowing for a mass flux of the ions.^{7–12}

Figure 1: Dry $\mathcal{B}_d$, initial hydrated $\mathcal{B}_o$, and actual $\mathcal{B}_t$ configuration of the body. It is worth noting that the deformation from $\mathcal{B}_d$ to $\mathcal{B}_o$ is spherical and stress-free.

The dry configuration of the material body is denoted with $\mathcal{B}_d$, a three-dimensional region of the Euclidean space $\mathcal{E}$, and with $\partial\mathcal{B}_d$ its boundary. The state of $\mathcal{B}_d$ is described by the motion f_d , see Figure 1. The motion is a smooth function that assigns to each material point $\mathbf{X} \in \mathcal{B}_d$ and time $t \in \mathcal{I}$ a place $\mathbf{x} \in \mathcal{E}$:

$$\mathbf{x} = f_d(\mathbf{X}, t) = \mathbf{X} + \mathbf{u}_d(\mathbf{X}, t), \quad (1)$$

Figure 2: The polymer membrane (purple) is sandwiched between flat and non-porous electrodes (orange). Top and bottom faces of the membrane correspond to the interfaces between the membrane and the top and bottom electrode.

where $\mathbf{u}_d$ represents the displacement vector from the material point $\mathbf{X} \in \mathcal{B}_d$ to the place $\mathbf{x} \in \mathcal{B}_t$. The region of space $\mathcal{B}_t \in \mathcal{E}$ occupied by the body represents the actual configuration of $\mathcal{B}_d$ at time t . It holds:

$$\mathbf{F}_d(\mathbf{X}, t) = \nabla f_d(\mathbf{X}, t) = \mathbf{I} + \nabla \mathbf{u}_d(\mathbf{X}, t), \quad (2)$$

for the gradient of the motion $\mathbf{F}_d$.

It is assumed that a stress-free state $\mathcal{B}_o$ is reached from the dry state $\mathcal{B}_d$ through a homogeneous swelling deformation f_o which identifies the initial configuration $\mathcal{B}_o$ attained from $\mathcal{B}_d$:

$$f_o(\mathbf{X}) = f_d(\mathbf{X}, 0), \quad \nabla f_o(\mathbf{X}) = \mathbf{F}_o(\mathbf{X}) = \mathbf{F}_d(\mathbf{X}, 0) = \lambda_o \mathbf{I}. \quad (3)$$

Moreover, $f_o(\mathbf{X}) = \mathbf{X} + \mathbf{u}_o(\mathbf{X})$ being $\mathbf{u}_o(\mathbf{X}) = \mathbf{u}_d(\mathbf{X}, 0)$ the displacement from $\mathcal{B}_d$ to $\mathcal{B}_o$. Therefore, a dry unloaded and constraint free membrane lays in a hydrated environment, and swells until an equilibrium state according to the well-known Flory-Rehner thermodynamics is attained:¹³

$$RT \left(\log \frac{J_o - 1}{J_o} + \frac{1}{J_o} + \frac{\chi}{J_o^2} \right) + \frac{G_d}{\lambda_o} \Omega = \mu_o, \quad \text{with} \quad J_o = \lambda_o^3, \quad (4)$$

being G_d the shear modulus of the dry polymer, $R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$ the universal gas constant, T the temperature, χ the dimensionless Flory parameter, Ω the volume of solvent (water) per unit mole (i.e. the inverse of the water molarity), and μ_o the chemical potential of the water inside the polymer that, at the equilibrium state, is equal to the chemical potential of the environment possibly depending on different factors such as relative humidity, temperature, pH, and other.

In the present paper, the water diffusion inside the membrane is neglected. The initial state $\mathcal{B}_o$ of the body is completely determined by the parameter λ_o ,⁶ such as $\lambda_o \geq 1$. Please, note that for $\lambda_o = 1$, $\mathcal{B}_o = \mathcal{B}_d$. Hence, to a dry membrane of size $(L_1, L_2, 2h)$ it corresponds a hydrated membrane of size $(\lambda_o L_1, \lambda_o L_2, 2\lambda_o h)$. The state variables of the electro-chemo-mechanical (ECM) model are the electric potential $\varphi : \mathcal{B}_o \rightarrow \mathcal{R}$, the mobile ion concentration $c : \mathcal{B}_o \rightarrow \mathcal{R}$ per unit freely swollen volume, and the (small) displacement $\mathbf{u} : \mathcal{B}_o \rightarrow \mathcal{V}$ from $\mathcal{B}_o$. They satisfy the balance equations of the mechanics, of the ions diffusion, and of the electrostatics:¹⁴

$$\nabla \cdot \mathbf{S} = \mathbf{0}, \quad -\nabla \cdot \mathbf{j} = \dot{c}, \quad \nabla \cdot \mathbf{d} = q \quad \text{in} \quad \mathcal{B}_o, \quad (5)$$

respectively. In equations (5), the relaxed-stress measure $\mathbf{S}$, the ion flux $\mathbf{j}$, and the electric displacement $\mathbf{d}$ have to be constitutively prescribed. Furthermore, q is the electric charge density defined as coulomb per unit of reference area. The expression $\dot{(\cdot)} = \partial/\partial t(\cdot)$ indicates the derivative with respect to the time. One species of mobile positive ions (cations) and one species of bound negative ions (anions) are considered within the membrane. Both ionic species have a valence number equal to one. Such a structure is representative of membranes made of Nafion,^{8,10,14–16} which are often employed in sandwiched-based structures as in Fig. 2. As

it is well-known, the balance equations show a first coupling between the electrical and chemical fields as it is assumed that the charge density q per unit freely swollen volume is delivered by the difference between the concentration c of the cations and the concentration c^- of the bound anions:

$$q = F(c - c^-), \quad (6)$$

being $F = 96485.33 \text{ C mol}^{-1}$ the Faraday constant. The concentration c_d^- of the bound negative ions per unit dry volume is constant. The concentration c^- of the bound negative ions per unit freely swollen volume is identified in such a way that

$$c^- dV_o = c_d^- dV_d \Rightarrow c^- = \frac{c_d^-}{J_o}, \quad (7)$$

being $J_o dV_d = dV_o$, where dV_d and dV_o are two infinitesimal volume elements related to $\mathcal{B}_d$ and $\mathcal{B}_o$, respectively. Equations (5) have to be equipped with suitable initial and boundary conditions, both of them define the electro-chemo-mechanical characteristics of the hydrated initial state $\mathcal{B}_o$. The initial conditions are set as follows:

$$\mathbf{u}(\mathbf{x}, 0) = \mathbf{0}, \quad c(\mathbf{x}, 0) = c^-, \quad \varphi(\mathbf{x}, 0) = 0. \quad (8)$$

Before specifying the boundary conditions, it is convenient to define the dry membrane with respect to a cartesian reference system $\{o; \mathbf{i}_1, \mathbf{i}_2, \mathbf{i}_3\}$ with o as the middle point of the membrane (see Fig. 2) and the corresponding coordinate system (x, y, z) . With this, the plate-like body $\mathcal{B}_d = \mathcal{P}_d \times (-h, h)$ is introduced, being $\mathcal{P}_d$ a square-like portion of size L_β ($\beta = 1, 2$) in the plane of unit normal $\mathbf{i}_3$. Note that, being $\mathbf{F}_o$ a spherical deformation, the hydrated membrane $\mathcal{B}_o$ keeps the plate-like shape: $\mathcal{B}_o = \mathcal{P}_o \times (-\lambda_o h, \lambda_o h)$. It is set $\partial \mathcal{B}_o = \mathcal{M} \cup \mathcal{P}_o^+ \cup \mathcal{P}_o^-$, with $\mathcal{M}$ the lateral boundary of the membrane $\mathcal{B}_o$, $\mathcal{P}_o^+$ and $\mathcal{P}_o^-$ the top and bottom faces of the membrane, respectively, corresponding to the interfaces between the membrane and the upper and lower electrode. The problem with the following boundary conditions is solved:

$$\mathbf{u} = \mathbf{0}, \quad -\mathbf{j} \cdot \mathbf{i}_3 = 0, \quad \varphi = \frac{1}{2} \bar{\varphi}, \quad \text{on } \mathcal{P}_o^-, \quad (9)$$

$$\mathbf{S} \mathbf{n} = -\bar{\sigma} \mathbf{i}_3, \quad -\mathbf{j} \cdot \mathbf{i}_3 = 0, \quad \varphi = -\frac{1}{2} \bar{\varphi}, \quad \text{on } \mathcal{P}_o^+, \quad (10)$$

$$\mathbf{S} \mathbf{n} = \mathbf{0}, \quad -\mathbf{j} \cdot \mathbf{n} = 0, \quad -\nabla \varphi \cdot \mathbf{n} = 0, \quad \text{on } \mathcal{M}, \quad (11)$$

being $\mathbf{n}$ the unit normal to the boundary $\partial \mathcal{B}_o$. The superscript $\bar{(\cdot)}$ indicates an input value. Equations (9), (10) and (11) represent a set of Dirichlet and Neumann boundary conditions for the mechanical, chemical and electrical field, respectively. These boundary conditions represent a polymeric membrane sandwiched between flat electrodes under constant applied voltage conditions. Mechanical boundary conditions always refer to a clamp at the lower surface $\mathcal{P}_o^-$, whereas at the upper surface $\mathcal{P}_o^+$ a constant pressure field $\bar{\sigma} > 0$ or a clamp $\bar{\sigma} = 0$ is considered.

The constitutive prescriptions for the mechanical, chemical and electrical field are borrowed from Refs. 6, 8, 14, where they are derived within a thermodynamically consistent framework. A free energy is chosen in order to describe the full thermodynamics of the system, and to fulfill the requirement that the dissipation inequality holds along any electro-chemo-mechanical process. Following Ref. 14, it is assumed that the small deformation $\mathbf{E} = \text{sym } \nabla \mathbf{u}$ admits an additive decomposition in an inelastic component $\check{\mathbf{E}}$ and an elastic component $\mathbf{E}_e$:

$$\mathbf{E} = \check{\mathbf{E}} + \mathbf{E}_e, \quad \text{with: } \mathbf{E} = \text{sym } \nabla \mathbf{u} = \frac{1}{2}(\nabla \mathbf{u} + \nabla \mathbf{u}^T), \quad \check{\mathbf{E}} = \frac{1}{3} \alpha (c - c^-) \mathbf{I}. \quad (12)$$

being $\check{\mathbf{E}}$ related to the change in ion concentration and α a parameter which is often identified with the hydrophilicity coefficient of the cations. It is worth noting that equations (12) represent an internal constraint relating two state variables of the problem; the electric displacement $\mathbf{d}$ and the ion flux $\mathbf{j}$ get the following form:

$$\mathbf{d} = \varepsilon_r \varepsilon_0 \mathbf{e} = -\varepsilon_r \varepsilon_0 \nabla \varphi, \quad \mathbf{j} = -D \left[\nabla c + \frac{c}{RT} (F \nabla \varphi + \alpha \nabla p) \right], \quad (13)$$

respectively. In the equations (13), ε_r is the relative dielectric permittivity, $\varepsilon_0 = 8.8542 \times 10^{-12} \text{ C V}^{-1} \text{ m}^{-1}$ is the vacuum dielectric permittivity, $\mathbf{e}$ is the electric field, D is the diffusion coefficient and p is the pressure which is defined as:

$$p = -\frac{1}{3} \text{tr}(\mathbf{S}). \quad (14)$$

The stress $\mathbf{S}$ turns out as linearly depending on the elastic deformation $\mathbf{E}_e$ through an isotropic elasticity tensor $\mathbb{C}$ as

$$\mathbf{S} = \mathbb{C}\mathbf{E}_e = 2G\mathbf{E}_e + (K - \frac{2}{3}G) \text{tr}(\mathbf{E}_e)\mathbf{I}, \quad (15)$$

with the elastic moduli G and K depending on the hydrated state $\mathcal{B}_o$ through the following expressions⁶

$$G = \frac{G_d}{\lambda_o}, \quad K = -\frac{1}{3}G + \frac{RT}{\Omega} \frac{J_o - 2\chi(J_o - 1)}{J_o^2(J_o - 1)}. \quad (16)$$

3. FROM FULLY COUPLED TO REDUCED MODELS

The mathematical model presented in Sec. 2 is solved at different levels of details with the aim to identify the simplest not trivial modeling of a single element of a proton-exchange membrane. In Section 3.1, the fully coupled model is implemented in a commercial finite element code and solved for the state variables ϕ , c , and $\mathbf{u}$ for two different test cases: (i) constraining the lower face $\mathcal{P}_o^-$ by clamps and keeping free and unloaded the upper face $\mathcal{P}_o^+$ and the mantle $\mathcal{M}$, and (ii) constraining the lower face $\mathcal{P}_o^-$ by clamps, keeping free and unloaded the mantle $\mathcal{M}$, and considering an external constant pressure over the upper face $\mathcal{P}_o^+$. This last condition aims at mimicking the working condition of one element of a battery embedded in a stack of elements. The two working conditions employed in this work are identified as (i) “clamp – free” (CF) where $\bar{\sigma} = 0$, and (ii) “clamp – constant stress” (CS), see Fig. 3. The same two conditions have been considered in a reduced model based on the aforementioned three-dimensional formulation and on the idea that the relevant electro-chemistry occurs across the thickness as in Ref. 17, see Sec. 3.2. Finally, in Sec. 3.3, a bar model with a distortive field is presented and discussed.¹⁸

3.1 Finite Element Implementation of the Fully Coupled Model

A membrane that firstly swells without constraint to chemically equilibrate with the external environment whose chemical potential is $\mu_o = 0$ is considered. Then, the swollen membrane $\mathcal{B}_o$ is bonded on its lower face to a rigid substrate. At time zero, a difference in voltage is applied between the two faces of the membrane. Two different cases are investigated (i) the top face is kept free and unloaded (CF), and (ii) a constant weight is applied on the top face of the membrane (CS). Mobile ions can diffuse within the membrane, which deform and stress along the process.

Within the finite element method framework, the differential balance equations (5) are satisfied in an average sense by converting them into an integral equation (called also weak form) and by finding $\mathbf{u}$, c , and φ such that, for all test fields $\tilde{\mathbf{u}}$, $\tilde{c}$, and $\tilde{\varphi}$, it holds:

$$\int_{\mathcal{B}_o} \mathbf{S} \cdot \nabla \tilde{\mathbf{u}} dV_o = \int_{\partial \mathcal{B}_o} \tilde{\mathbf{u}} \cdot \mathbf{S} \mathbf{n} dA_o, \quad (17)$$

$$\int_{\mathcal{B}_o} (\dot{c}\tilde{c} - \mathbf{j} \cdot \nabla \tilde{c}) dV_o = - \int_{\partial \mathcal{B}_o} \tilde{c} (\mathbf{j} \cdot \mathbf{n}) dA_o, \quad (18)$$

$$\int_{\mathcal{B}_o} (F(c - c^-)\tilde{\varphi} + \mathbf{d} \cdot \nabla \tilde{\varphi}) dV_o = \int_{\partial \mathcal{B}_o} \tilde{\varphi} (\mathbf{d} \cdot \mathbf{n}) dA_o, \quad (19)$$

where first the integration by parts and then the divergence theorem are employed. By using the backward Euler method for the time derivative and by performing a discretization procedure through linear shape functions for the test fields, a system of nonlinear algebraic equations is obtained. The nonlinearity is solved by using the Newton-Raphson iteration scheme. The minimization of the residual allows to obtain a well approximated solution of the electro-chemo-mechanical problem.

3.2 1D Reduced Model

As the in-plane dimensions of the gel are much larger than its thickness, the ions flux is mainly directed in the thickness direction and is a function of the position z and of the time t . The displacement in the thickness direction, $u_3(z, t)$, and the electric potential $\phi(z, t)$, are also functions of time and of position. It is assumed that, as the ions migrate into the network, the in-plane dimensions of the membrane remain unchanged, whereas in-plane stresses are generated. So, the problem is studied assuming that:

$$\mathbf{u} = \hat{\mathbf{u}} + u_3 \mathbf{i}_3, \quad \hat{\mathbf{u}} = 0 \quad \text{and} \quad u_3 = u_3(z, t). \quad (20)$$

Furthermore, $c = c(z, t)$ and $\varphi = \varphi(z, t)$, and with this, also ions flux and electric displacement are going to be identified with their components $j_3(z, t)$ and $d_3(z, t)$. Combining the balance equation (5)₃ and the constitutive relations (13)₁, it gives

$$c = c^- + \frac{1}{F} d'_3 = c^- + \frac{\varepsilon_r \varepsilon_0}{F} e'_3, \quad (21)$$

where $(\cdot)' = \partial(\cdot)/\partial z$. A time derivative of equation (21) leads to the following expression:

$$\dot{c} = \frac{1}{F} \dot{d}'_3 = \frac{\varepsilon_r \varepsilon_0}{F} \dot{e}'_3. \quad (22)$$

By inserting equation (13)₂ into equation (5)₂, and by using equation (22),

$$FD \left[c' + \frac{c}{RT} (F\varphi' + \alpha p') - \frac{\varepsilon_r \varepsilon_0 \dot{e}'_3}{FD} \right]' = 0, \quad (23)$$

it is obtained. Being $\hat{\mathbf{u}} = \mathbf{0}$, the visible strain $\mathbf{E}$ is completely determined by the component along the thickness direction: $\mathbf{E} = E_{33}(\mathbf{i}_3 \otimes \mathbf{i}_3) = u'_3(\mathbf{i}_3 \otimes \mathbf{i}_3)$. With this, the stress $\mathbf{S}$ only exhibits diagonal components S_{11} , S_{22} , and S_{33} :

$$S_{11} = S_{22} = \left(K - \frac{2}{3}G \right) u'_3 - K\alpha(c - c^-), \quad (24)$$

$$S_{33} = \left(K + \frac{4}{3}G \right) u'_3 - K\alpha(c - c^-), \quad (25)$$

where equations (15), (12)₁ and (12)₃, are employed. Furthermore, the balance equation of mechanics (5)₁ reduce to $S'_{33} = 0$. Assuming that a constant weight per unit area is applied over the top surface of the membrane, the balance equation becomes $S_{33} = S_{33}(\lambda_o h) = \bar{\sigma}$ (see the boundary condition (10)₁); hence, from equation (25):

$$u'_3 = \alpha \frac{K}{(K + \frac{4}{3}G)} (c - c^-) + \frac{1}{(K + \frac{4}{3}G)} \bar{\sigma}. \quad (26)$$

It is also convenient to define the pressure p in terms of the concentration by using equations (24), (25), and (26):

$$p = -\frac{1}{3} \text{tr}(\mathbf{S}) = \alpha \frac{4KG}{3(K + \frac{4}{3}G)} (c - c^-) - \frac{K}{(K + \frac{4}{3}G)} \bar{\sigma}. \quad (27)$$

With this, all the terms in equation (23) can be expressed in terms of the electric field and it holds

$$\left((\varepsilon_r \varepsilon_0 e'_3) - D \left((\varepsilon_r \varepsilon_0 e''_3) - \frac{F^2 c^-}{\varepsilon_r \varepsilon_0 RT} (\varepsilon_r \varepsilon_0 e_3) + \frac{4KG\alpha^2 c^-}{3RT(K + \frac{4}{3}G)} (\varepsilon_r \varepsilon_0 e''_3) \right) \right)' = 0, \quad (28)$$

where, following Ref. 17, the terms $e'_3 e_3$ and $e'_3 e''_3$ are neglected. This means that part of the migrative term and the pressure term in the Nernst-Planck equation (13)₂ are not taken into account. In steady-state conditions $\dot{e}_3 = 0$, therefore by using the wall boundary condition for the ion flux (see the boundary conditions (9)₂, (10)₂, and (11)₂), it is possible to write equation (28) as follows:

$$(\zeta^2 e'' - \iota^2 e) = (-\varphi'' + \vartheta^2 \varphi)' = 0 \Rightarrow (\varphi'' - \vartheta^2 \varphi) = \varkappa, \quad (29)$$

being $\varkappa$ an integration constant, whereas ζ , ι and ϑ are constants which depend on the material parameters

$$\zeta^2 = \left[1 + \frac{4KG\alpha^2 c^-}{3RT(K + \frac{4}{3}G)} \right] \varepsilon_r \varepsilon_0, \quad \iota^2 = \frac{F^2 c^-}{RT}, \quad \vartheta = \frac{\zeta}{\iota}. \quad (30)$$

The non homogeneous second order PDE (29)₂ can be analytically solved as

$$\varphi(z, t) = -\frac{\bar{\varphi}}{2} \frac{\sinh(\vartheta z)}{\sinh(\vartheta \lambda_o h)}, \quad (31)$$

where the boundary conditions (9)₃ and (10)₃ as well as the conservation of the electric charge, determining that $\varphi'(-\lambda_o h) = \varphi'(\lambda_o h)$, are employed. Starting from equation (31), it is possible to define all the other electro-chemo-mechanical fields:

$$e_3(z) = -\varphi'(z, t) = \frac{\bar{\varphi} \vartheta}{2} \frac{\cosh(\vartheta z)}{\sinh(\vartheta \lambda_o h)}, \quad (32)$$

$$c(z) = c^- - \frac{\varepsilon_r \varepsilon_0}{F} e_3'(z) = c^- + \frac{\bar{\varphi} \varepsilon_r \varepsilon_0 \vartheta^2}{2F} \frac{\sinh(\vartheta z)}{\sinh(\vartheta \lambda_o h)}, \quad (33)$$

$$u_3(z) = \frac{K}{(K + \frac{4}{3}G)} \left[\frac{\bar{\sigma}}{K} (z + \lambda_o h) + \frac{\alpha \bar{\varphi} \varepsilon_r \varepsilon_0 \vartheta}{2F} \frac{(\cosh(\vartheta z) - \cosh(\vartheta \lambda_o h))}{\sinh(\vartheta \lambda_o h)} \right], \quad (34)$$

where the expression of the displacement u_3 is obtained by integrating the kinematic relation $E_{33} = u_3'$, and by using equation (26) together with the boundary condition (11)₁, namely $u_3(-\lambda_o h) = 0$. The space evolution of the electro-chemo-mechanical parameters presented in this section holds for two different configurations (i) “clamp – free” where $\bar{\sigma} = 0$, and (ii) “clamp – constant stress”. It should be pointed out that the electro-chemical problem does not depend on the constant weight $\bar{\sigma}$, however the mechanical problem is influenced by $\bar{\sigma}$.

3.3 1D Bar Model

The bar model allows to set an uncoupled point of view of the electro-chemo-mechanical physics occurring along the thickness of the polymer membrane. Due to the applied difference in voltage, the mobile ions diffuse determining a distortion which is related to the one-dimensional mechanics. The equation is formally analogous to the one used in the thermal analysis of elastic structures:¹⁸

$$E_Y A u_3''(z) - \frac{\alpha E_Y A}{3} c'(z) = 0, \quad (35)$$

where E_Y is the Young's modulus, A is the cross section area of the bar, and where distributed longitudinal forces are neglected. The electro-chemical field (namely $\varphi(z)$, $e_3(z)$ and $c(z)$) comes from the reduced 1D model already described in Sec. 3.2. An expression for the displacement $u_3(z)$ can be obtained by integrating equation (35), together with the expression of the concentration in equation (33):

$$u_3(z) = \frac{\alpha \bar{\varphi} \varepsilon_r \varepsilon_0 \vartheta}{6F} \frac{(\cosh(\vartheta z) - \cosh(\vartheta \lambda_o h))}{\sinh(\vartheta \lambda_o h)} + \frac{\bar{\sigma}}{E_Y} (z + \lambda_o h), \quad (36)$$

Figure 3: Sketch of the considered configurations: a) “clamp – free” (CF), and b) “clamp – constant stress” (CS). The computational domain corresponds to the polymeric membrane (purple). At the interfaces between the electrodes (orange) and the membrane, an input voltage is applied while wall conditions arise for the ionic flux.

Table 1: Material parameters, initial and boundary conditions employed in the ECM model proposed in the present work.

Parameter	Value	Unit
E_Y	2.2×10^8 ^{a,b}	N m^{-2}
ν	0.3 ^{a,b}	-
λ_o	1.25 ^c	-
Ω	1.8×10^{-5} ^c	$\text{m}^3 \text{mol}^{-1}$
α	1.18×10^{-5} ^b	$\text{m}^3 \text{mol}^{-1}$
χ	0.2 ^c	-
T	300 ^a	K
D	4.5×10^{-9} ^d	$\text{m}^2 \text{s}^{-1}$
ε_r	2×10^9 ^b	-
c^-	1185 ^e	mol m^{-3}
$\bar{\varphi}$	0.01	V
$\bar{\sigma}$	-7×10^4 ^f	N m^{-2}

^a Ref. 22, ^b Ref. 14, ^c Ref. 6,
^d Ref. 23. ^e Ref. 17. ^f Ref. 20.

where the boundary conditions

$$u_3(-\lambda_o h) = 0, \quad E_Y A \left[u_3'(\lambda_o h) - \frac{\alpha}{3} (c(\lambda_o h) - c^-) \right] = \bar{\sigma} A, \quad (37)$$

are employed. As for the 1D reduced model, this formulation is suitable for two different configurations (i) “clamp – free” (CF) where $\bar{\sigma} = 0$, and (ii) “clamp – constant stress” (CS).

4. NUMERICAL INVESTIGATION

The behavior of a polymer membrane is investigated under constant input voltage conditions, and by considering wall conditions for the ionic flux. The membrane is clamped at the lower surface, while is either free or loaded with a constant weight per unit area at the upper surface. The boundary and initial conditions employed in the present work (see equations (9), (10) and (11)) are representative for (i) a polymeric membrane included in a fuel cell stack,¹⁹ (ii) a pouch cell in a battery pack under a clamping load,²⁰ and (iii) a lithium-ion battery cell under a certain state of charge and mechanical compression loading.²¹ It is assumed that the membrane has size $L_1 = L_2 = 0.002$ m and thickness $2h = 1.8 \times 10^{-4}$ m.^{8,22}

The three levels of investigation discussed in Section 3 are performed: (i) the three-dimensional fully coupled multi-physics model (3D ECM), see Sec. 3.1, is numerically solved within a finite element framework by using the commercial tool COMSOL Multiphysics, (ii) an analytical steady-state solution for the main electro-chemo-mechanical variables is obtained by using a one-dimensional reduced approach (1D reduced), see Sec. 3.2, finally, (iii) a simple approach based on the bar theory with a distorsive field (1D bar) is employed in order to obtain an analytical expression of the displacement in steady-state conditions, see Sec. 3.3.

The parameters employed in the model are listed in the Table 1 and briefly discussed in Sec. 4.1. Then, in Sec. 4.2, the steady-state profiles of the electro-chemo-mechanical variables are discussed with reference to the two different configurations investigated: CF and CS.

4.1 Parameter analysis

The material parameters are summarized in Table 1, and used for both the configurations CF and CS. The dry membrane thickness $2h$ shows values which are usually employed for Nafion membranes in fuel cells.²⁴ The relative dielectric permittivity ε_r is a critical value for polymeric membranes: authors have used values with circa nine orders of magnitude of difference.^{14,15} In this work, this parameter is assumed as in Ref. 14 and its dependence on the hydrated state of the membrane is neglected. Furthermore, the hydrophilicity coefficient

Figure 4: Steady-state profile of (a) ion concentration c , and of (b) electric potential φ delivered by the 3D ECM model (dotted line with circle markers) and the 1D reduced model (solid line). The same trend is observed for both the configurations CF and CS.

α is adopted as for Nafion membranes employed in ionic polymer metal composites,¹⁴ even if, a parametric investigation may be useful to predict a much more accurate value. The applied voltage $\bar{\varphi}$, as well as the applied pressure field $\bar{\sigma}$, can be regarded as characteristic values that are usually adopted for fuel cell working conditions. The mechanical properties of the Nafion membranes are given in dry conditions in terms of Young's modulus E_Y and Poisson's number ν ,^{14,22} from which the dry shear G_d and bulk K_d modulus can be easily determined. Then, the wet mechanical parameters are obtained according to the equations (16).

4.2 Steady-state results

The steady-state profiles of the main electro-chemo-mechanical fields are drawn on the hydrated thickness $2\lambda_o h$ and, in each figure, dotted vertical lines are inserted to emphasize the difference between the dry thickness $2h$ of the membrane and the hydrated thickness.

The steady-state profiles of the concentration c and of the electric potential φ are shown in Fig. 4a and Fig. 4b, respectively. As expected, the same trend is observed for the configuration CF and CS. The positive ions move towards the electrode where a negative potential is applied; in the bulk, the ion concentration is unchanged compared to the initial concentration, while at the membrane/electrode interface high gradients develop for both electro-chemical degrees of freedom. The boundary conditions on the applied voltage are captured by both models, the 3D ECM and the 1D reduced. A good agreement is shown between the fully coupled model solved numerically and the one-dimensional model analytically solved. Finally, it should be pointed out that small discrepancies can be observed in the bulk evolution of the electric potential, due to the fact that the one-dimensional model neglects parts of the nonlinear terms related to the potential gradient within the equation of the ionic flux.

Figure 5, shows the steady-state profiles of the component u_3 of the displacement along the z -direction. The “clamp – free” (CF) and the “clamp – constant stress” (CS) working conditions are discussed in Fig. 5a and 5b, respectively, where the outcomes from the three levels of investigation (3D ECM, 1D reduced and 1D bar) are considered. The tip displacement at $z = \lambda_o h$ is zero for the CF configuration, while is negative for the CS configuration because of the applied compression force. In the CF configuration, the membrane shows first a compression and then an extension without changing the reference thickness ($2h\lambda_o$). The high gradients at the membrane/electrode interfaces are in accordance with the equation (26), where it can be observed that the

Figure 5: Steady-state profile of the displacement u_3 for the configuration (a) “clamp – free” (CF), and (b) “clamp – constant stress” (CS). Each level of investigation is taken into account: (i) the 3D ECM model (dotted line with circle markers), (ii) the 1D reduced model (solid line), and (iii) the 1D bar model (dashed line).

displacement and the concentration profiles are related. The effect of the electro-chemical degrees of freedom on the displacement profile is less pronounced for the CS configuration, nevertheless, a change in the gradient of the displacement can be noticed. A good agreement is observed between the 3D ECM model and the 1D reduced model; on the contrary, the outcomes of the bar model greatly differ.

5. CONCLUSION AND OUTLOOK

A three-dimensional and time-dependent electro-chemo-mechanical model has been proposed for the investigation of the polymer membranes. Furthermore, an analytical expression for the main electro-chemo-mechanical parameters in steady-state conditions is obtained through either (i) a reduced one-dimensional model or (ii) an approach inspired by the bar theory. The initial and boundary conditions considered in this paper are typically employed in literature^{19–21} to investigate the behavior of membranes within fuel cell stacks or battery packs.

The 3D ECM model is capable of well describing the electro-chemo-mechanical behavior of polymeric membranes, while the analytical approaches (namely, 1D reduced and 1D bar) allow to gain a rapid insight into the dependence between the main material parameters and the response of the membrane.

The proposed multi-field model can be considered as an excellent starting point for further research, especially (i) the modeling of the water uptake/intake between the reference and actual configuration, and (ii) large deformations within a nonlinear mechanics context.

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