



Multi-physic 3D dynamic modelling of polymer membranes with a proper generalized decomposition model reduction approach

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ABSTRACT

Modelling ionic conduction polymeric proton-exchange membranes at the heart of fuel cells requires the solution of highly nonlinear partial differential equations in very thin domains. Recently, proper generalized decomposition methods have emerged as particularly promising methods for this type of problems. This paper introduces the basics of this novel class of approaches and highlights their potential benefits.

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1. Introduction

Proton-exchange membranes (PEMs) are key-components of PEMFCs, a promising class of fuel cells (FC), which use ionic conduction polymers as electrolyte between the electrocatalysts layers. PEMs allow ion transport while preventing the passage of electrons, a key feature of electrochemical devices in order to force electrons to flow in the load. The membranes become ion-conductive when they are sufficiently hydrated, allowing the flow of protons after these have been produced at the electrochemical activity sites from the ionization of fuels such as hydrogen and methanol. In optimal conditions the proton conductivity can reach values as high as 20 S/m at 100 °C, which is a fairly good value for ions, but a very poor one if compared with the electronic conductivity in metals, being in the order of common pure semiconductors. In order to reduce the inherent voltage and power losses such electrolytes must be built as thin as possible but avoiding that the manufacturing inaccuracies produce too high relative thickness fluctuations.

Electrochemical activity sites generate current densities, which can reach values of 10^4 A/m² so that device currents in the order of 500 A require membrane cross sections of $0.2 \text{ m} \times 0.2 \text{ m}$ with typical thicknesses in the order of $2\text{--}3 \times 10^{-4}$ m. The numerical simulation of such a domain, with aspect ratio exceeding 10^3 , involves severe size problems: a regular hexahedral tessellation with ten elements in the thickness direction implies 10^9 nodes in the whole domain

which can only be faced with parallel computing and multiprocessor computers [1]. As a further concern, depending on the transient timescale, a large number of timesteps may be needed in order to accurately compute time evolutions.

1.1. Charge transport in a polymer exchange membrane

Modelling the physical problem rises a number of numerical problems. The PEM conductivity depends on the water content of the membrane and on its temperature according to strongly nonlinear equations. In turn the water content is distributed inside the membrane according to a diffusion equation with boundary conditions which are related to the water vapor pressure at anode and cathode faces [2]. On the other hand the temperature depends on the membrane bulk (i.e. Joule) and boundary (i.e. electrochemical kinetic) losses and on thermal diffusion.

Proton conducting polymers, i.e. the ionomers used as electrolyte in PEMFCs, present a dielectric behavior when completely dry, but can soak up water and when they are hydrated enough they become conductive, allowing proton transport, i.e. ionic conduction, while preventing electron migration [3]. The most popular and important of this class of materials is persulfonated polytetrafluoroethylene (PTFE, i.e. Teflon), commercially known as Nafion, a Du Pont patent, which has a backbone structure similar to PTFE but functionalized with sulfonic acid groups, which provide charge sites for proton transport [2]. Protons combine with water forming hydronium complexes which detach from sulfonic acid groups moving inside the ionomer. In this way conduction relies mainly on the water vehicle mechanism (i.e. protons migrate being attached

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to water molecules). As a first approximation, which is valid for a wide range of realistic operation conditions, according to experimental data provided by Springer et al. [2], proton conductivity σ can be considered a linear function of the water content. The latter can then be expressed by the hydration λ , which is the ratio of the number of water molecules to the number of sites available for proton transport (i.e. sulfonic acid groups). The distribution of λ , and consequently of $\sigma = \alpha \cdot \lambda$, inside the membrane varies according to Fick's first law, which allows to relate conductivity to the water molar flow \mathbf{N} [mol/m²s] as [4]:

$$\mathbf{N} = -\frac{D_w c_{sa}}{\alpha} \nabla \sigma \quad (1)$$

where D_w [m²/s] is the water diffusivity in the membrane, $c_{sa} = 1970$ mol/m³ is the sulfonic acid concentration and $\alpha = 51.93$ S/m, according to the experimental data provided in Ref. [2]. The dynamics of the water molar flow \mathbf{N} is described by Fick's second law, which, expressed in terms of σ , reads:

$$\nabla \cdot \mathbf{N} + \frac{c_{sa}}{\alpha} \frac{\partial \sigma}{\partial t} = 0 \quad (2)$$

Thus, combining (1) and (2), the equation to be solved in order to compute the conductivity of the membrane is:

$$\frac{\partial \sigma}{\partial t} - \nabla \cdot D_w \nabla \sigma = 0 \quad (3)$$

Membrane conductivity is coupled with the temperature through a double dependence, i.e. directly and through D_w and both are based on quantum-mechanical statistical parameters related to the activation barriers:

$$\sigma(\lambda, T) = \alpha \lambda e^{(W_{ai}/k)((1/303)-(1/T))}, \quad D_w = D_0 e^{-(W_{aw}/kT)} \quad (4)$$

where k is Boltzmann's constant, W_{ai} is the activation barrier energy ($(W_{ai}/k) = 1268$ K for ions hopping in Nafion), and D_0 is a diffusivity reference value. A further difficulty is posed by the shortage of experimental data for determining the parameters in the previous relationship, which results in the need to run more simulations in order to explore parameter values consistent with the available measurements.

1.2. Numerical challenges

Computing the conductivity and current distributions is a challenging complex multi-physics problem based on of partial differential equations including complicated material laws. The resulting numerical problem incurs severe issues when faced with the finite element method and may even be intractable when the conventional discretization techniques are applied [5]. These issues can be addressed through various approaches to dimension reduction in state and parameter space. Recently, a new family of numerical techniques, known as proper generalized decomposition (PGD) has been introduced [6,7]. They constitute an appealing strategy for reducing the computer resources and the calculation costs based on reducing drastically the number of degrees of freedom that the functional approximations involve. In fact PDG models scale linearly with the dimension of the space in which the model is defined instead of the exponential growth characteristic of common mesh-based discretization strategies. PGD-type methods are based on factorization and separation of variables. This paper is aimed at introducing the basics of this type of approach to a subset of the equations presented in Ref. [5] and to show the potential benefits of PGD for this class of problems. With the aim of highlighting the fundamental aspects of PGD, the presentation given in this

paper assumes a constant material parameter D_w , in an isothermal membrane, which reads:

$$\mathcal{L}(\sigma) = \frac{\partial \sigma}{\partial t} - D_w \nabla^2 \sigma = 0 \quad (5)$$

where \mathcal{L} is the operator containing the time and space derivatives.

2. The PGD method applied to the 3D transient conductivity equation

Following the PGD approach the solution to (5) is approximated by a series of factorized terms:

$$\begin{aligned} \sigma &= \sum_{i=1}^{N+1} \sigma_i(x, y, z, t) = \sum_{i=1}^{N+1} X_i(x) Y_i(y) Z_i(z) T_i(t) \\ &= \sum_{i=1}^N X_i(x) Y_i(y) Z_i(z) T_i(t) + R_x(x) R_y(y) R_z(z) S(t) \end{aligned} \quad (6)$$

which allow to separate the single space and time variables, using as many terms as needed to reach the required accuracy.

Since each function depends on a single variable the prime symbol ($'$) is used for the derivative with respect to the corresponding variable with no risk of ambiguity.

The solution of (5) can be found with the weighted residual approach by solving the corresponding problem

$$\iiint \sigma^* \mathcal{L}(\sigma) dx dy dz dt = 0 \quad \forall \sigma^* \quad (7)$$

Assuming that the first N terms of the series expansion of σ are known and only R_x , R_y , R_z and S have to be found, and the weight function can be written as:

$$\sigma^* = R_x^* R_y R_z S + R_x R_y^* R_z S + R_x R_y R_z^* S + R_x R_y R_z S^* \quad (8)$$

where R_x , R_y , R_z and S will be determined by an alternating simple iteration scheme (i.e. R_x , R_y , R_z and S are computed one-by-one cyclically assuming the remaining ones to be known), which usually converges in a few steps, as will be shown by numerical examples.

2.1. Determination of S

Assuming that R_x , R_y and R_z are known ($R_x^* = R_y^* = R_z^* = 0$), after inserting (6) and (8) in (7) the problem reduces to the determination of S such that

$$\begin{aligned} \iiint \int S^* R_x R_y R_z \left(\sum X_i Y_i Z_i T_i' - D_w \sum (X_i'' + Y_i'' + Z_i'') T_i \right. \\ \left. + R_x R_y R_z S' - D_w (R_x'' + R_y'' + R_z'') S \right) dx dy dz dt = 0 \quad \forall S^* \end{aligned} \quad (9)$$

In this expression the quantities which depend on x , y and z only can be grouped and evaluated. Defining:

$$\alpha = \int R_x^2 dx \int R_y^2 dy \int R_z^2 dz \quad (10)$$

$$\beta_x = \int R_x R_x'' dx \int R_y dy \int R_z dz \quad (11)$$

$$\beta_y = \int R_x dx \int R_y R_y'' dy \int R_z dz \quad (12)$$

$$\beta_z = \int R_x dx \int R_y dy \int R_z R_z'' dz \quad (13)$$

$$\xi_i = \int R_x X_i dx \int R_y Y_i dy \int R_z Z_i dz \quad (14)$$

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