Stochastic Methods for Parameter Estimation of Multiphysics Models of Fuel Cells

P. Alotto, M. Guarnieri

Dipartimento di Ingegneria Industriale, Università di Padova, Via Gradenigo 6/a, 35131 Padova, Italy

piergiorgio.alotto@unipd.it, massimo.guarnieri@unipd.it

Abstract— **The accurate modeling of complex multiphysical devices and systems is a crucial problem in engineering. Such models are usually characterized by highly nonlinear equations and depend on a high number of parameters which often cannot be directly measured. In this paper two stochastic optimization techniques are adapted and compared to the solution of such challenging problems in the case of a reversible fuel cell system.**
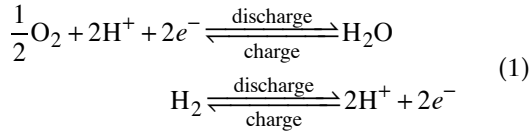
*Index Terms—***Optimization methods, Parameter estimation, Fuel cells.**

I. Introduction

A fundamental problem in engineering is the accurate modeling of complex multiphysical devices, which are often characterized by highly nonlinear equations including parameters which are very hard, or even impossible, to measure directly. In particular, Fuel Cells (FCs) are systems of such type, and their models include parameters with very wide ranges depending on the specific cell type and mode of operation. The problem of their identification with stochastic optimization methods has been addressed only very recently and the literature on the subject is rather scarce [1]. Here we briefly introduce a model for a reversible fuel cell, show the most critical parameters of the system and solve the inverse problem of identifying them with two stochastic optimization techniques, showing the feasibility of the proposed approach.

II. Reversible Fuel Cell Model

A multiphysical model of a reversible polymer exchange membrane (PEM) fuel cell (R-PEMFC) using the same equations for both working modes, i.e. the charge (electrolyzer-mode) and discharge (fuel-cell-mode) operations [2] is presented here briefly. Two half-reactions occur at the negative and positive electrodes, respectively:

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} H_2O$$

$$H_2 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} 2H^+ + 2e^- \tag{1}$$

Electrodes are separated by the PEM, that allows the flow of protons while forcing electrons in the external circuit. The reversible voltage is expressed by the Nernst equation:

$$E = E^0 + \frac{\Delta\hat{s}}{nF}(T - 298.15\,) + \frac{T}{f}ln\frac{c_{H_2}\,c_{O_2}{}^{0.5}}{c_{H_2}^0\,c_{O_2}^0{}^{0.5}} \tag{2}$$

where $\Delta\hat{s} = -44.34\,\text{J K}^{-1}\text{mol}^{-1}$ is the molar entropy change, c/c^0 the activity of the reagent hydrogen and oxygen, $f = nF/R = 11607\,\text{K V}^{-1}$ with $n = 2$ the charge carriers as in (1), F the Faraday constant, and R the gas constant. In load conditions the voltage changes due to different types of losses:

$$v = E - \Delta v_{aa} - \Delta v_{ac} - \Delta v_m - \Delta v_{ca} - \Delta v_{cc} \tag{3}$$

where *aa* and *ac* stand for anodic and cathodic activation losses, *m* for the ohmic losses in the membrane, and *ca* and *cc* for anodic and cathodic concentration losses. The rate of charge separation and recombination at anode and cathode are modeled by the Butler-Volmer equation:

$$\partial_t\sigma_g = j_0\left(\frac{c_R}{c_{R0}}e^{\alpha f\,\Delta v_a/T} - \frac{c_P}{c_{P0}}e^{-(1-\alpha)f\,\Delta v_a/T}\right) \tag{4}$$

where ∂_t is the time partial derivative. σ_g is in [C/s·cm²] like a current density and it actually is such in steady state conditions. c_{ik}/c_{ik0} are the reagent concentrations normalized to the bulk undisturbed values c_{i0}. The relation $\alpha = \alpha_{oi}T$ is used for the transfer coefficient α. The current density j_0 depends on temperature according to Arrhenius equation:

$$j_0 = j_0^*\,e^{\frac{W_{aj}}{R}\left(\frac{1}{T_0^*} - \frac{1}{T_0}\right)} \tag{5}$$

where W_{aj} is the activation barrier. Proton $\partial_t\sigma_g$ (and electron $-\partial_t\sigma_g$) change rate can differ from the current densities originating from the anode and cathode catalyst layers due to charge accumulation according to:

$$\nabla_\Sigma\cdot\boldsymbol{j} + \partial_t\sigma = \partial_t\sigma_g \tag{6}$$

where $\nabla_\Sigma\cdot$ is the surface divergence, $\boldsymbol{j}$ the current density, and σ the accumulated proton and electron surface charge densities. The losses due to reagent concentrations are modeled by the limit current density, i.e. the maximum value that causes the concentration to vanish:

$$j_L = nFK\bar{c}_R \tag{7}$$

with $\bar{c}_R$ the average flow channel reagent concentration and K the mass transfer coefficient :

$$K = \left(\frac{d_{fc}}{Sh\,D} + \frac{\delta}{D_{eff}}\right)^{-1} \tag{8}$$

δ is the diffusion layer thicknesses, D_{eff} its effective diffusivity, while the first term can be neglected. A concentration-related steady state voltage drop expression for each electrode can be derived from (2) and (4). In order to account also for secondary effects, the following expression is used:

$$\Delta v_c = \frac{\kappa_c T}{f}ln\frac{1}{1 - j/j_L} \tag{9}$$

κ_c is a dimensionless empirical parameter. Concentrations at both catalyst layers depend on the gas molar flows N, and thus on $\boldsymbol{j} = nF\boldsymbol{N}$, according to Fick's law $\boldsymbol{N} = -D_{eff}\Delta c$, yielding:

$$c_R = \bar{c}_R - \frac{j}{nFK} \tag{10}$$

When properly hydrated a PEM is a protonic conductor with ohmic behavior, so that Δv_m of Eq. 3 is:

$$\Delta v_m = \frac{d_m}{\gamma_m} j \qquad (11)$$

where d_m is the PEM thickness and γ_m its conductance :

$$\gamma_m = \gamma_m^* \, e^{\frac{W_{am}}{R}\left(\frac{1}{T^*}-\frac{1}{T}\right)}$$
$$\gamma_m^* = \gamma_m(T^*) = \left(-3.26\cdot10^{-3} + 0.5193\lambda\right) \qquad (12)$$

with, T*=303 K and W_{am} the activation energy. The hydration $\lambda = c_w/c_{sa}$ is the ratio between water and sulfonic acid concentrations, $(0.02\leq\lambda\leq0.22)$. λ is assumed to vary linearly across the PEM from λ_a at anode to λ_c at cathode, and thus its average value is used in (12). λ_a and λ_c are defined by the water activity a_w of the gases at the catalyst layers according to:

$$\lambda = \begin{cases} 4.3\cdot10^{-5} + 0.18a_w - 0.399a_w^2 + 0.36a_w^3; 0 \leq a_w \leq 1 \\ 0.14 + 0.014\left(a_w - 1\right); \qquad\qquad 1 \leq a_w \leq 3 \end{cases} \qquad (13)$$

A major effect impacting on the efficiency is fuel crossover, i.e. hydrogen flowing through the PEM towards the cathode without oxidizing at the anode. It is accounted for by increasing the left hand side of (4) for the cathode by the crossover term:

$$\partial_t \sigma_{gH} = \frac{nFD_H}{d_m} c_H \qquad (14)$$

D_H is the diffusivity of hydrogen inside the PEM and c_H its concentration at the anode catalyst layer as in (10) (assuming zero value at the cathode side). The temperature dependence of D_H according to Arrhenius equation is modeled as:

$$D_H = D_H^* \, e^{\frac{W_{aH}}{R}\left(\frac{1}{T^*}-\frac{1}{T}\right)} \qquad (15)$$

with $D_H^* = D_H(T^*)$ and W_{aH} the activation energy. Gas molar flows at both diffusion layers must sustain the crossover hydrogen cathodic reaction, so that the equivalent current density in the Δv_c of. (9) is also increased by $j_x = \partial_t \sigma_{gH}$.

TABLE I
CRITICAL PARAMETERS SUBJECT TO OPTIMIZATION

Parameter	Equation	Range	Nominal value
$\overline{c}_R$ anode	10	$[1.0\bullet10^{-10}, 1.0\bullet10^{-5}]$	$2.0\bullet10^{-6}$
$\overline{c}_R$ cathode	10	$[1.0\bullet10^{-10}, 1.0\bullet10^{-5}]$	$1.5\bullet10^{-6}$
j_0^* anode	5	$[1.0\bullet10^{-10}, 1.0\bullet10^{1}]$	0.1
j_0^* cathode	5	$[1.0\bullet10^{-10}, 1.0\bullet10^{1}]$	$1.0\bullet10^{-3}$
a_w	13	$[0.1, 0.95]$	0.9

The most critical parameters are summarized in Table I together with their possible range and with the nominal value used in the numerical experiments.

III. STOCHASTIC OPTIMIZATION METHODS AND RESULTS

Stochastic optimization methods are widely used in the area of electromagnetics and the recent relevant literature is vast. They are especially suited for multimodal and noisy functions over large search spaces, which makes them particularly appealing for the problem at hand. The main drawback of such methods is the high number of objective function evaluations needed for convergence, however due to particular type of modeling adopted for the R-PEMCF, such drawback is not significant in this context and computational times are in the order of few tens of seconds. We have applied two of the most well-known metaheuristics, namely Particle Swarm Optimization (PSO) [3] and Differential Evolution (DE)[4], developed in previous work and suitably adapted.

The objective function is the maximum difference between simulated measurements and the model output, where the the former were obtained by inserting the nominal values of Table 1 in the model and adding a 5% random noise to the model output. Table II shows the success rate of PSO and DE, where an optimization run is considered successful if the optimal objective function value is below 0.05. The same table also shows the best, worst and average optimal solutions obtained by the two optimizers, showing the clear superiority of DE.

TABLE II
COMPARISON OF PSO AND DE

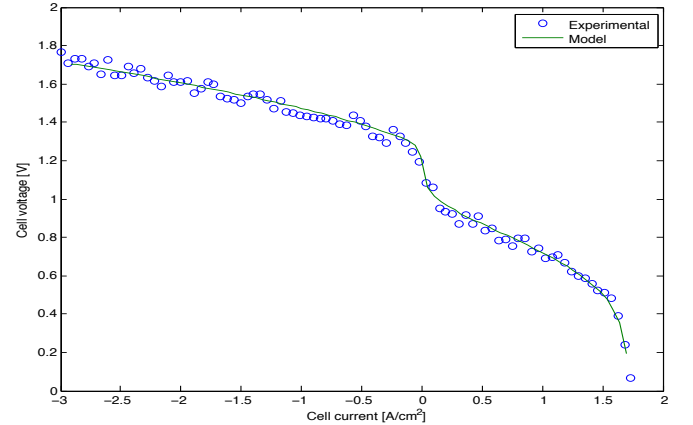| Algorithm	Success rate	Best	Mean	Worst
PSO	2%	0.044	0.104	0.122
DE	62%	0.035	0.069	0.126

Fig. 1: Example of a successful identification run by DE

IV. CONCLUSIONS

Two stochastic optimization methods have been applied to a parameter estimation problem in fuel cell modeling. Results indicate that the applied methodology can successfully solve the problem. The extended paper will provide more details regarding the implementation of the optimizers as well as the application of the proposed methodology to experimental data of a real PEM fuel cell.

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