Journal of Power Sources 332 (2016) 249–264

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

A selective hybrid stochastic strategy for fuel-cell multi-parameter identification

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HIGHLIGHTS

- A method is presented for obtaining more FC material parameters at once.
- It is based on a proper combination of two stochastic optimization algorithms.
- It makes use of a FC multiphysics performance model.
- Dependences on temperature, pressure and humidification are taken into account.
- An example of application is given and critical issues are discussed.

ARTICLE INFO

Article history:
Received 2 June 2016
Received in revised form
26 August 2016
Accepted 22 September 2016

Keywords:
Fuel cell
In situ characterization
Material characterization
Multiphysics modeling
Multiple identification
Stochastic methods

ABSTRACT

The *in situ* identification of fuel-cell material parameters is crucial both for guiding the research for advanced functionalized materials and for fitting multiphysics models, which can be used in fuel cell performance evaluation and optimization. However, this identification still remains challenging when dealing with direct measurements. This paper presents a method for achieving this aim by stochastic optimization. Such techniques have been applied to the analysis of fuel cells for ten years, but typically to specific problems and by means of semi-empirical models, with an increased number of articles published in the last years. We present an original formulation that makes use of an accurate zero-dimensional multi-physical model of a polymer electrolyte membrane fuel cell and of two cooperating stochastic algorithms, particle swarm optimization and differential evolution, to extract multiple material parameters (exchange current density, mass transfer coefficient, diffusivity, conductivity, activation barriers …) from the experimental data of polarization curves (i.e. *in situ* measurements) under some controlled temperature, gas back pressure and humidification. The method is suitable for application in other fields where fitting of multiphysics nonlinear models is involved.

1. Introduction

1.1. Fuel cell perspectives

As electricity sources which do not undergo the Carnot cycle limitations, Fuel Cells (FCs) are appealing for a number of applications within the future energy framework. Solid Oxide FCs (SOFCs) and Molten Carbonate FCs (MCFCs), working at high temperatures (around 600 °C), promise to be competitive in the stationary middle-to-micro combined heat and power production (CHP). Proton Exchange Membrane fuel cells (PEMFCs) constitute the more promising technology for mobility, with early applications in niche sectors (e.g. forklifts, golf carts, submarines). As regards road mobility, PEMFC-powered urban bus fleets, capable of longer ranges than batteries, have been tested and introduced in big cities (e.g. London, Hamburg, Barcelona, Stockholm, Oslo, Porto, Stuttgart, Amsterdam, Luxemburg, Madrid, Aberdeen, Reykjavík, and Perth). In these years, the electric car market is expanding, but battery-powered models still lack competitiveness as regards range, recharge time, lifetime, and cost. PEMFC-powered cars, capable of longer ranges and faster refueling, are now entering mass production. The Hyundai ix35 (FC version of the Tucson SUV), commercialized since 2013, is the first of them and has been followed in 2014–5 by the Toyota Mirai FCV, whose two 122-liter 70-MPa hydrogen tanks provide a 650 km range. Honda and Mercedes-Benz are going to sell their models FCX Clarity II (35-MPa

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http://dx.doi.org/10.1016/j.jpowsour.2016.09.131
0378-7753/

tanks for 390-km range) and F-Cell (70-MPa tanks for 678-km range) within 2016 and 2017, respectively. As regards devices working at lower power levels, the sensational spread of portable electronics has been backed by batteries with high energy density, but small-sized Direct Methanol Fuel Cells (DMFCs) are emerging as a competitive alternative for assuring extended durations. Success in all these sectors relies on the availability of more efficient, more durable and cheaper next-generation FCs based on new materials and architectures.

1.2. FC material characterization

Since fuel cells present a stratified structure of thin layers made of different materials, analyzing their behavior requires the full characterization of these materials, i.e. the determination of a their chemical, physical, thermal, and electrical parameters [1]. Unfortunately, they are hard to measure in real operating conditions. These physical parameters are also needed in FC models, which allow the fast exploration of different operating scenarios and can be used in the research of optimized structural design and operating conditions [2,3]. The systems of equations involved (Nernst equation, Butler-Volmer equation, Darcy's equation, Fourier's law, Ohm's law, …) are strongly non-linear, causing the models to be extremely sensitive to parameter variations and uncertainties. Careful *ex situ* measurements can be performed by means of a number of diagnostic techniques, e.g. cyclic voltammetry with the thin-film rotating ring-disc electrode (CV-TF-RRDE) setup, electrochemical impedance spectroscopy (EIS), and broadband electrical spectroscopy (BES) [4–8]. However, the transferability of their results to operative fuel cells raises a number of issues. Conversely, *in situ* measurements can provide meaningful operational values, but very few, often complicated and cumbersome, techniques are available to determine a limited number of parameters, e.g. EIS, neutron radiography, and voltammetric and chronoamperometric approaches in the "driven-cell" mode [4,5,9].

1.3. Numerical optimization search approach

A different approach consists in multiple parameter identification from a rich sample of experimental data obtained at different values of temperature, and gas pressure and humidity. Unfortunately, this approach is not so easy to implement, because the problem becomes increasingly difficult as the number of parameters increases, resulting in the *curse of dimensionality* issue [10]. This challenge can be faced with mathematical optimization, which typically consists in a minimization or maximization problem [11]. In the former case, given a function f (called fitness, objective, quality, or cost function) that maps a domain A (search space) of an n-dimensional Euclidean space into real numbers, optimization aims at finding the element x_0 of A such that $f(x_0)$ is smaller than every other $f(x)$ for x in A:

$$\begin{array}{ll} \text{given} & f(x): \quad A \to \mathbf{R} \quad A \subseteq \mathbf{R}^n \\ \text{seek} & x_o \in A: \quad f(x_o) \le f(x) \quad \forall x \ne x_o \end{array} \tag{1}$$

The optimization problem can be similarly formulated as a mathematical maximization. When using mathematical optimization for model parameter identification, x is the n-dimensional vector whose elements are the unknown parameters and $f(x)$ consists of a proper error among the computed performance values provided by a parameter-based model and measured performance data. Optimization problems are typically constrained, in the sense that A is given with a number of constraints and is also typically burdened by model non-linearity, as is the case of an FC model, which results in the non-convexity of f and consequent local minima x^* [12]:

$$f(x^*) \le f(x) \quad \|x - x^*\| \le \delta \tag{2}$$

Moreover, large problems lead to high computational cost. Given the problems of curse of dimensionality, presence of local minima and computational costs, smart strategies can find good solutions, if not the absolute best one, which actually may be impossible to find. Although the *no-free-lunch* theorem shows that "any two optimization algorithms are equivalent when their performance is averaged across all possible problems" [13], efficient optimizers exist which allow to solve our specific problem of finding only a domain-specific solution.

Stochastic methods have been introduced in the analyses of FCs in the last decade and their use has been strongly increasing in the last three years. The researches published so far aim at exploring the capability of stochastic methods in achieving good fittings of PEMFC polarization curves and resort to simplified empirical PEMFC models, used as black boxes. Those stochastic methods demonstrate to be efficient at that aim, since their results depend on some optimization parameters which must be trimmed at the experimental polarization curves. In these conditions, fitting a set of empirical parameters to match a given polarization curve is not a hard task for numerical optimizers, but the usefulness of the results is limited. By using a proper number of unknown parameters (5–7), they provide enough flexibility for fitting purposes without introducing *duplicity problems* (i.e. multiple fitting solutions which can appear when many unknowns are sought). However, duplicity is not crucial, because empirical parameters have no direct physical meaning. Conversely, the algorithm that we present, built over an early investigation on the capability of stochastic methods to deal with FCs [14], aims at identifying several physical parameters of the materials of a PEMFC by means of an optimization approach. At this aim, we use a detailed multi-physical performance model that employs such parameters and takes into account some physical control quantities [15].

In the following sections, we first present the PEMFC performance model, consisting of non-linear equations, which provides the computed performance (the PEMFC polarization curves) at different values of physical control quantities (temperature, gas pressure and humidity) making use of the unknown parameters. Then, we present the *selective hybrid stochastic algorithm* that we have developed for identifying the unknown parameters. It consists of a *hybrid stochastic method* complemented with a *selective strategy* for coping with the duplicity problem. Finally, an example of multi-parameter identification is presented.

2. PEMFC multiphysics performance model

The model for the stochastic identification must strike a balance between opposite requirements. On one hand it should be extremely rich in order to be able to represent the complete behavior of the cell, i.e. a multiphysical, three-dimensional model, described by partial differential equations (PDEs) and characterized by a large number of physical parameters which can capture the detailed distribution of the physical quantities inside the cell and their time evolution. On the other hand it should be sufficiently simple to be suitable for being included in a stochastic optimization loop, i.e. the model should be numerically computable in a very short time, considering the CPU power at hand, and it should be characterized by a relatively small number of parameters in order to avoid the *curse of dimensionality* issue. Here we resort to a zero-dimensional stationary model that avoids PDEs and their inherent computational burden in order to match these conflicting requirements and to run the algorithm on a standard PC.