Journal of Power Sources 326 (2016) 417–427

Contents lists available at ScienceDirect

Journal of Power Sources

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

Proton exchange membrane fuel cell model for aging predictions: Simulated equivalent active surface area loss and comparisons with durability tests

C. Robin [a, b, c, d], M. Gérard [a, *], M. Quinaud [a], J. d'Arbigny [d], Y. Bultel [b, c]

[a] Univ. Grenoble Alpes, CEA, LITEN, F-38054, Grenoble, France
[b] Univ. Grenoble Alpes, LEPMI, F-38000, Grenoble, France
[c] CNRS, LEPMI, F-38000, Grenoble, France
[d] Zodiac Aerospace, F-78370, Plaisir, France

HIGHLIGHTS

- Prediction by simulation of PEM fuel cell lifetime.
- Multiscale modelling of catalyst dissolution and global loss of performance.
- Reconstruction of active surface area loss by model inversion.
- Prediction and validation of current density evolution during aging.
- Validation by two 2000-h experimental stack aging tests.

ARTICLE INFO

Article history:
Received 17 February 2016
Received in revised form
3 July 2016
Accepted 5 July 2016
Available online 15 July 2016

Keywords:
PEM fuel cell
Durability test
Modeling
ECSA loss
Lifetime prediction
Degradation

ABSTRACT

The prediction of Proton Exchange Membrane Fuel Cell (PEMFC) lifetime is one of the major challenges to optimize both material properties and dynamic control of the fuel cell system. In this study, by a multiscale modeling approach, a mechanistic catalyst dissolution model is coupled to a dynamic PEMFC cell model to predict the performance loss of the PEMFC. Results are compared to two 2000-h experimental aging tests. More precisely, an original approach is introduced to estimate the loss of an equivalent active surface area during an aging test. Indeed, when the computed Electrochemical Catalyst Surface Area profile is fitted on the experimental measures from Cyclic Voltammetry, the computed performance loss of the PEMFC is underestimated. To be able to predict the performance loss measured by polarization curves during the aging test, an equivalent active surface area is obtained by a model inversion. This methodology enables to successfully find back the experimental cell voltage decay during time. The model parameters are fitted from the polarization curves so that they include the global degradation. Moreover, the model captures the aging heterogeneities along the surface of the cell observed experimentally. Finally, a second 2000-h durability test in dynamic operating conditions validates the approach.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Fuel cells are a promising technology to address energy issues in various fields. For transportation, Proton Exchange Membrane Fuel Cells (PEMFC) offer many advantages compared to classic thermal engines, such as a better efficiency, a good dynamic response, a cleaner and less noisy energy conversion [1]. However, two main barriers are still remaining for a widespread commercialization of PEMFC: high components' costs and moderate durability [2]. Fuel cells aging concerns for transportation may be one of the most challenging issue to be dealt with. Indeed, the strong dynamics of the power profiles together with constraining operating conditions are most of the time incompatible with a high lifetime of PEMFC.

Due to the variety of materials used inside a fuel cell, various degradation mechanisms can occur [3–5]. These mechanisms can be reversible (temporary performance loss) or irreversible. Among

* Corresponding author.
E-mail address: mathias.gerard@cea.fr (M. Gérard).

http://dx.doi.org/10.1016/j.jpowsour.2016.07.018
0378-7753/© 2016 Elsevier B.V. All rights reserved.

Nomenclature

Acronyms

BoL	Beginning of Life
ECSA	Electrochemical Catalyst Surface Area
EoT	End of Test
GDL	Gas Diffusion Layer
MEA	Membrane Electrode Assembly
PEMFC	Proton Exchange Membrane Fuel Cell
STEM	Scanning Transmission Electron Microscopy

Symbols

C_j	concentration of the species j (mol m^{-3})
dn_k	variation of the platinum particles number of the population k (−)
E_{GT}	Gibbs-Thomson energy (J mol^{-1})
F	Faraday constant (C mol^{-1})
i	local current density (A m^{-2})
I_{cell}	fuel cell current (A)
k	direct reaction constant (mol m^{-2} s^{-1})
M_j	molar mass for the species j (kg mol^{-1})
m_j	mass for the species j (kg)
n	number of exchanged electrons (−)
P^0	standard pressure (Pa)
P_j	partial pressure for the species j (Pa)
r	radius (m)
R	gas constant (−)
R_{ohm}	specific ohmic resistance (ohm.m^2)
S	electrode surface (m^2)
T	temperature (K)
t	time (s)
U_{cell}	cell voltage (V)
U_{rev}	reversible cell voltage (V)
v	surface chemical velocity (mol m^{-2} s^{-1})
v_{diss}	dissolution rate of the platinum particle (mol m^{-2} s^{-1})

Greek letters

α	reaction transfer coefficient (−)
β_k	semi-empirical electrochemical reaction coefficients (V or V K^{-1} or Ω.m^2 or m)
ΔG	variation of free Gibbs energy (J)
ΔG_s	variation of free enthalpy required for a platinum atom extraction (J)
ΔG_{elec}	variation of free enthalpy required for a platinum atom oxidation (J)
ΔG_{des}	variation of free enthalpy required for leaching of Pt^{2+} (J)
$\Delta N_k(t)$	cumulated variation of the particles number in the population k (−)
$\Delta\chi$	local potential at the inner layer (V)
γ	surface tension (J m^{-2})
η	over potential (V)
ρ_j	density for the species j (kg m^{-3})
σ	protonic conductivity (S m^{-1})
τ_{degr}	degradation rate of the Electrochemical Surface Area (−)

Subscripts

a	anode
c	cathode
m	membrane

the latter, the polymer membrane degradation is likely to be the one mostly responsible for the failure of PEMFC [6]. Mechanical and thermal membrane degradations could be modeled [7], however they have little effects on the fuel cell performances evolution during operation, except at the very end of the cell lifetime when its permeation current increases dramatically. It is a very sudden phenomenon which could be correlated also with the Membrane-Electrode Assembly (MEA) initial fabrication defects and the bipolar plate mechanical constraints. Therefore, the mechanical and chemical membrane degradations with the estimation of a sudden failure are beyond the scope of this paper. Another critical degradation mechanism in PEMFC concerns the catalyst layers and especially the active surface area loss during fuel cell operation. For instance, the irreversible losses can be due to carbon support corrosion, catalyst dissolution/redeposition and catalyst layer micro-porous structure modification [8]. Conversely to the membrane degradation, these mechanisms affect directly the fuel cell performances with time but not directly a fuel cell failure. Degradation of Gas Diffusion Layers (GDL) and bipolar plates can also be observed but they seem to be of less value regarding fuel cells durability [7].

The understanding of degradation mechanisms by modeling has been conducted intensively with very different approaches [7]. However, the prediction of the fuel cell lifetime under dynamic cycles is less described even if some studies focus on it. In particular, Fowler et al. [9] have introduced a parameter in the semi-empirical electrochemical response of their model to take into account an Electrochemical Surface Area (ECSA) loss. Soltani et al. [10] have used some durability tests to build empirical laws giving the evolution of global parameters (potential, temperature, etc.) with time. However, this approach is not able to give any physical information neither on the degradations mechanisms that occur nor on their locations at the cell surface. As an original modeling approach, Jouin et al. [11–12], have used neural networks to predict the fuel cell lifetime after a learning phase during the first hundred hours of a test. Conversely to these approaches, Kulikovsky [13] has built a purely theoretical model to study catalyst and GDL degradation effects on the fuel cell performance and especially on the current density distribution. Pohl et al. [14] have used differential equations to take into account the membrane degradation and the evolutions of the current density distribution with time. The authors couple this approach with the dual time theory in order to dissociate the time scales proper to the different degradation mechanisms. Finally, Dhanushkodi et al. [15] have modeled a simplified carbon corrosion mechanism which have been successfully validated on several Accelerated Stress Tests. In all these studies however, the simulated data concerning aging phenomena are scarce. No results are given on the location of the various degradations on the cell surface.

The objectives of this work are to build a PEM fuel cell predictive model able to simulate the fuel cell aging with time and to explain the behavioral evolutions with local degradation mechanisms. A 2000-h durability test is used in this study to help building the degradation module and to validate it.

2. Experimental part

2.1. Description of the 2000-h durability test with steady operating conditions

A stack equipped with 30 large-area cells has been operated during 2000 h with steady operating conditions. The 220 cm^2 MEAs

Download English Version:

https://daneshyari.com/en/article/7727847

Download Persian Version:

https://daneshyari.com/article/7727847

Daneshyari.com