17^{th} INTERNATIONAL SYMPOSIUM on
POWER ELECTRONICS - Ee 2013

NOVI SAD, SERBIA, October 30^{th} - November 1^{st}, 2013

A VOLTAGE DEGRADATION MODEL FOR PEM FUEL CELLS

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Abstract: Durability of proton exchange membrane fuel cells (PEMFCs) is one of the major obstacles to the comercialization of these systems for statianary and mobile applications. A reliable mathematical model allows a better understanding of the parameters that affect the PEMFC system's performance. In addition, the time and cost are reduced in the analysis and design of fuel cell systems. The model presented is a generalized electrochemical degradation model with voltage degradation (ageing) terms. The objective of the modeling effort presented in this paper is to model the observed behavior in performance, not to mechanistically model the degradation mechanisms. The objective was to develop a semi-empirical model that would simulate the performance of fuel cells without extensive calculations. The present model can be used to investigate the influence of process variables for design optimization of fuel cells, stacks, and complete fuel cell power systems. The model has been validated with data from a 500 h durability test of a singe cell.

Key Words: ***PEM fuel cell/ Durability/ Voltage degradation modelling***

1. INTRODUCTION

The energy and pollution crises are fast becoming a major issue around the world. As a consequence, new renewable and clean energy power sources must be considered. A fuel cell (FC) utilizes the chemical energy of hydrogen and oxygen to generate electricity without generating pollution. The by-products are simply pure water and heat [1]. The chemical reactions occurring at the anode and the cathode of a FC are the following:

Anode reaction: $H_2 \rightarrow 2H^+ + 2e^-$,

Cathode reaction: $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$.

The global reaction in a FC is therefore:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O.$$

There are several types of FCs, which are characterized by the electrolyte used. One of the most promising is the proton exchange membrane fuel cell (PEMFC). PEMFCs are an attractive technology due to their high energy density, rigid and simple structure, low operating temperature and fast start-up characteristics [1].

Fuel cell based power generation systems are expected to become more widespread, such as stationary power plants and portable power sources. Stationary fuel cells can be used as an uninterruptible or back-up power supply systems or as distributed generation (DG) sources [2]. PEM fuel cells show great promise for use as DG sources. Compared with other DG technologies, such as wind and photovoltaic generation, PEM fuel cells have the advantage that they can be placed at any site in a distribution system, without geographic limitations, to achieve the best performance. PEMFCs are also used for mobile and portable applications. Electric vehicles are another major application of PEM fuel cells [3, 4]. The increased desire for vehicles with lower emission has made PEM fuel cells attractive for transport applications since they emit essentially no pollutants and have high-power density and quick start.

3. DEGRADATION

The main barriers to market acceptance of PEM fuel cells are: endurance and reliability [5, 6]. Voltage degradation will be the main factor governing the life of the FC stack in terms of operating time, performance and reliability. The voltage degradation rate is normally a good indicator of a fuel cell state of health. It is usually in the range of 1–10 μV/h [5]. Failure of a FC is degradation below threshold value for the voltage, or other parameters such as efficiency or power. It is important to note that degradation must be accommodated in control systems. The most important parameters in electrical power systems are reliability and life expectancy.

The goal of this paper is the development of a generalized electrochemical degradation model in voltage degradation (ageing) terms. The development of the model and a better understanding of the degradation mechanisms will be of great interest for the development of the control system for the FC. Users need to be able to estimate the life span of a FC.

The main parameters known to influence PEM FC performance and life are: water management, corrosion of the catalytic layers and membrane degradation.

Water management is of vital importance to ensure stable operation, high efficiency and to maintain the power density of PEM fuel cells in the long run. On one hand it is important to keep the membrane humidified for high proton conductivity, because the membrane's conductivity is directly related to its water content. On the other hand accumulation of too much water also impacts performance and lifetime of the fuel cell [5, 6].

Corrosion of the electrocatalyst layers is one fundamental mechanism that strongly influences performance in the long run and is a major obstacle in commercialization of PEM fuel cells [5]. Corrosion of the catalyst is frequently addressed in the existing literature and is one of the better understood degradation mechanisms of PEM fuel cells. CO contamination is important when reformat gas is used.

Degradation of the membrane is probably among the main factors reducing the lifetime of PEM fuel cells [6]. Chemical stability of the membrane is critical to fuel cell's long life. In the PEM fuel cells membrane degrades more rapidly, especially in automotive applications due to potential cycling, frequent start-up and shut-down phases. The operational history of the FC will has a great influence on degradation and performance.

4. MATHEMATICAL MODEL

Much work has been done on modeling of PEM fuel cell performance, but few models address voltage degradation over time. Two main modeling approaches can be found in the literature.

The first approach includes mechanistic models, which aim to simulate the heat, mass transfer and electrochemical phenomena encountered in fuel cells. These models focus on modeling specific components of the fuel cell, while others aim to present a comprehensive simulation of the entire cell or stack. These models intend to explain the fundamental processes occurring in fuel cell systems and, therefore, serve as a tool for the design and optimization of the individual cell components.

The second approach includes models that are based on empirical or semi-empirical equations, which are applied to predict the effect of different input parameters on the voltage–current characteristics of the fuel cell, without examining in depth the physical and electrochemical phenomena involved in fuel cell operation.

Many mechanistic and empirical models can be found in literature and the complexity of these models varies [7-11]. Amphlett et al. [10, 11] developed a semi-empirical electrochemical model for a PEMFC combining theoretically derived differential and algebraic equations with empirically determined relationships. The model takes into account the main variables of the FC operation: the operating temperature, the current density, cathode and anode pressures. Other model parameters are the cell active area and membrane thickness [10].

The expression for the voltage of a single cell in a FC stack is given by:

$$V_{cell} = E_{Nernst} + \eta_{act\,A} + \eta_{act\,C} + \eta_{ohmic}\,, \qquad (1)$$

where: E_{Nernst} is the thermodynamic (open-circuit) potential of the cell, $\eta_{act\,A}$ is the anode activation overvoltage (a measure of the voltage loss associated with the anode), $\eta_{act\,C}$ is the cathode activation overvoltage (measure of the voltage loss associated with the cathode) and η_{ohmic} is the ohmic overvoltage, a measure of the IR losses associated with the proton conductivity of the polymer electrolyte and electronic internal resistances. The three overvoltage terms in Eq. 1 are all negative and represent reductions from E_{Nernst}, under normal operating conditions, the actual output voltage of a PEMFC is determined by irreversible voltage losses, present within the PEMFC, represented by V_{cell}.

In order to have a single expression of the activation overvoltages, Amphlett et al. combined the anode and cathode overpotentials and gave them in a parametric form:

$$\eta_{act\,A+C} = \xi_1 + \xi_2 T + \xi_3 T \cdot \ln\left(C_{O_2}\right) + \xi_4 T \cdot \ln(i). \qquad (2)$$

The terms ξ_i are semi-empirical coefficients. The use of such semi-empirical coefficients gives a significant degree of flexibility when modeling a specific fuel cell. In equation 2: T is the cell temperature, *i* the cell current and C_{O_2} the oxygen concentration at the cathode membrane/gas interface. The terms ξ_i can be obtained by a fitting procedure based on the measured polarization curve of a single cell or a stack. At the same time, these coefficients have a significant mechanistic background.

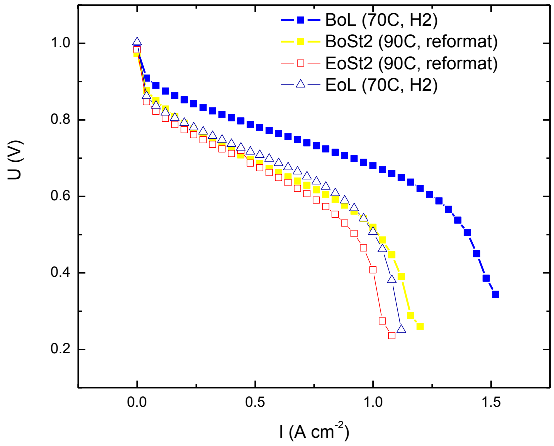

Fig. 1. Begining of Life and End of Life polarization curves for the tested cell measured at 70˚C with H_2 and Begining of Special test and End of Special test curves at 90˚C with reformate gas.

For developing a voltage degradation model the most important of these parameters is ξ_2 because a degradation term can be introduced in the equation:

$$\xi_2 = k_{cell} + 197 \cdot 10^{-6} \ln A + 4.3 \cdot 10^{-5} \ln C_{H_2}\,. \qquad (3)$$

M. W. Fowler et al. [11] showed that k_{cell} represents the measure of apparent catalytic activity. The actual surface area of the catalyst on the electrode that is in direct contact with the membrane will affect the performance of the cell.

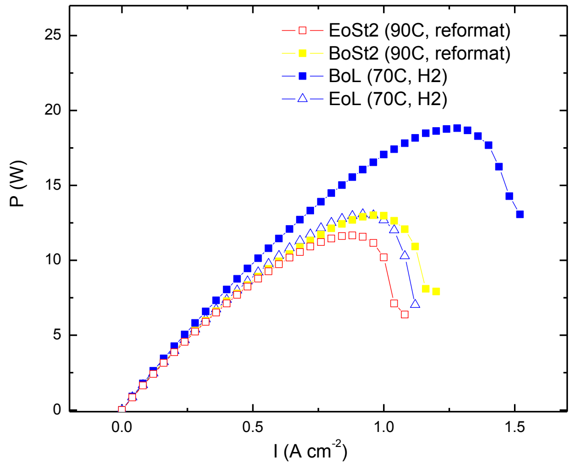

Fig. 2. Begining of Life and End of Life power curves for the tested cel lmeasured at 70˚C with H_2, Begining of Special Test and End of Special test power curves at 90˚C with reformate gas.

The active surface area or catalyst activity will be one of the main parameters that will degrade over the operational time of the cell. So it is this parameter that will change in the model to represent the degradation of the voltage associated with the loss of catalyst activity in the FC. The changes in catalytic activity are modeled by a first order degradation rate:

$$k_{cell} = k_0 \cdot \frac{age}{T} + k_1 . \qquad (4)$$

The ohmic losses result from the resistance to electron transfer in the collector plates and electrodes plus from the resistance to proton transfer in the polymer electrolyte membrane. These two terms together give the total cell internal resistance:

$$\eta_{ohmic} = -i \cdot \left(R^{electronic} + R^{proton} \right) = -i \cdot R^{internal} . \qquad (5)$$

For high purity graphite plates the $R^{electronic}$ is much less significant in comparison to R^{proton}, so we can neglect the electronic resistance [12]. The proton resistance is defined based on the membrane parameters:

$$R^{proton} = \frac{r_m \cdot l}{A} , \qquad (5)$$

where r_m is the membrane specific resistance (Ω cm) , l the thickness of the proton exchange membrane and A is the cell active area. For Nafion membranes, used in our experiments, the following empirical expression was proposed in literature:

$$r_m = \frac{181.6\left[1 + 0.03(i/A) + 0.062(T/303)^2 (i/A)^{2.5}\right]}{\left[\lambda - 0.634 - 3(i/A)\right] \exp\left\{3.25(T - 303)/T\right\}}$$

The total internal resistance is a complex function of temperature and current. The parameter λ is a function of membrane water content and as such it is strongly correlated with the overall cell management, but it is also a function of the cells age.

For the degradation parameter associated with the conductivity loss a simple linear relationship is proposed:

$$\lambda_{age} = \lambda_0 + \lambda_1 \cdot age , \qquad (6)$$

where 'age' represents the operating time of the cell (h).

5. EXPERIMENTAL

The model accuracy has been validated with data from a 500 h durability test of a singe cell with 25 cm^2 active area at 90^{o}C with reformat at the anode side (10ppm CO) and air at the cathode side. The test was conducted using the Hephas test station, programmable load and Hephas eLoad test software. It was shown that the model can be used to accurately predict the FC performance over time.

The model proposed in this paper is broad in applicability. Using this model it is possible to model FCs of any active area and Nafion membrane thicknesses over the range of operating current densities. The membrane used was Nafion XL with membrane thickness of 27.5 µm. The catalyst loading was:

Anode: PtRu Tanaka 0.4 mg/cm² Pt
Cathode: PtCo Tanaka 0.5 mg/cm² Pt

6. RESULTS AND DISCUSION

The polarization curve is used to examine the current-voltage characteristics over the whole range of current densities and is essential for studying fuel cell behavior. Figures 1 and 2 show BoL (Beginning of Life) and EoL (End of Life) polarization curves with hydrogen at the anode. The figures also show BoSt (Beginning of Special test) and EoSt (End of Special test) curves. BoSt and EoSt were measured at the beginning and end of the durability test conducted at the cell temperature of 90˚C with reformate gas. The degradation in performance after 500h is evident from these curves. Model validation involves the comparison of model results with experimental data, primarily for the purpose of establishing confidence in the model. To validate the mathematical model presented in the preceding section, comparisons were made to the experimental data for a single cell operated for 500h continuously is presented in figure 3.

The proposed model vas implemented in Matlab. The input parameters were: the cell temperature, membrane thickness and active area, the oxigen concentration at the cathode membrane/gas interface, the hydrogen concentration at the anode/gas interface. For the starting values of the semi-empirical parmeters ξ_i, k_0, k_1, λ_0 and λ_1 values published in referenc [9] were chosen. Then the parameters vere modified to better fit the cell voltage measured. MATLAB simulation results show voltage degradation of around 40µV/h. At this rate we can expect total cell degradation after around 7500 hours.

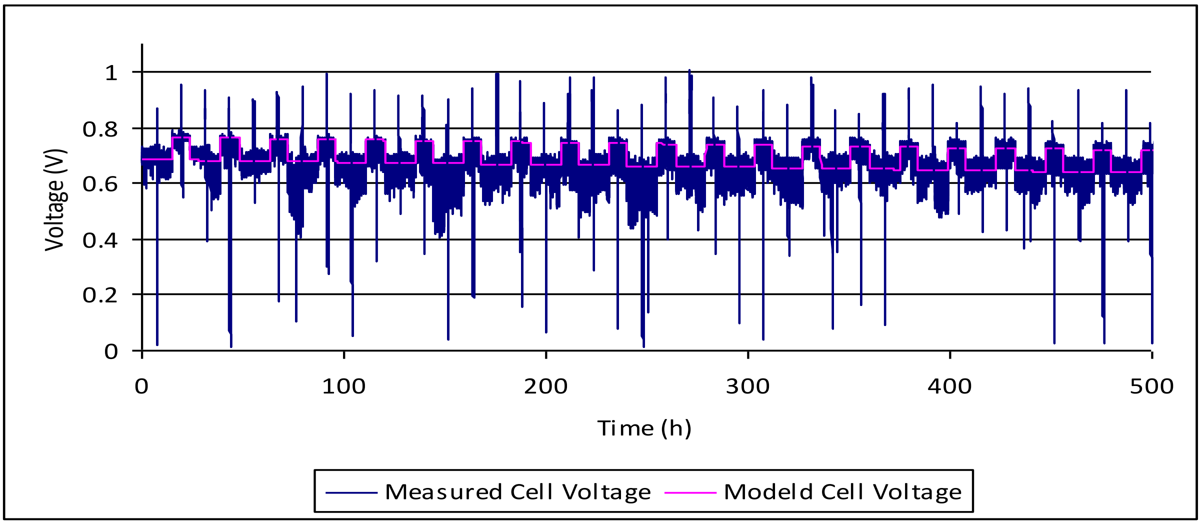

Fig. 1. Experimental data and the modeld cell voltage of the 500h durability test.

The proposed model can be extended over the life of the fuel cell so the cell performance can now be predicted as the cell ages. The mechanistic basis of the model gives it flexibility over a wide range of operating conditions.

7. CONCLUSIONS

In the proposed model the effective activity of the catalyst is considered using a semi-empirical parameter k_{cell} which is a function of the cells 'age' (the operating time of the cell). Also the resistance of the membrane (membrane water content) is considerd in a simplified way by a single semi-empirical parameter λ, also a function of the cell age.This paper als discusses the main couses that efect voltage derradation in a PEM FCs.

In conclusion we can say thet the presented voltage degradation model is a useful tool for simulation and design analysis of fuel cell power systems by adding parameters such as active cell area and membrane characteristics. And with the addition of an ageing parameter to the model, the model can be used in simulation of fuel cell performance over the life of the FC stack.

ACKNOWLEDGMENTS

The authors would like to thank the Ministry of Education, Science and Technological Development of the Republic of Serbia and FP7 JTI FCH-JU project “EURECA” (2012–2015), Grant Agreement n° 303024, for the financial support.

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