Load profile effect on durability of Proton Exchange Membrane Fuel Cells

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1. Introduction

Proton Exchange Membrane Fuel Cells (PEMFC) are a promising technology for substitution of hydrocarbon powerdrives and battery based electrical supply systems. However, below-required durability is still an important factor that hinders its widespread use, thus, novel operating approaches are required to surpass this shortcoming. The present abstract presents a line of research directed towards the of analysis and definition of load profile characteristics in order to design controlllers and operation strategies that optimize cell efficiency and durability. Degradation of the catalyst layer, commonly composed of platinum supported on carbon (Pt/C), mainly due to platinum loss by oxidation/dissolution and the resulting reduction of Electrochemical Active Surface Area (ECSA), is the main issue reducing the durability of PEMFC.

2. Experimental

2.1 Cell potential and catalyst evolution

The reaction kinetics of platinum (Pt) and the reactions affecting platinum stability within the cell are of mayor importance in order to study the process of cell degradation. Several models of Pt kinetics have been proposed [1,2,3], most of them agree on two pathways for Pt loss, based mainly on three reactions:

$$Pt \leftrightarrow Pt^{2+} + 2e^- \tag{1}$$

$$Pt + H_2O \leftrightarrow \mathrm{PtO} + 2H^+ + 2e^- \tag{2}$$

$$PtO + 2H^+ \rightarrow Pt^{2+} + 2H^+ + H_2O \tag{3}$$

A simulation model in MATLAB/SIMULINK has been developed based on this reaction kinetics. The results agree qualitatively with graphics of platinum oxide (PtO) evolution presented in [1,2], figure 1 shows the result of our model. A portion of the area below the PtO evolution curve defines the level of degradation suffered by the catalyst. Evolution of the electrochemical reactions (1) and (2) is strongly dependant on cell voltage, as several studies have shown, voltage cycling is one of the main conditions inducing PEMFC degradation [3,4].

2.2 Voltage profile features

In the literature, several semi-empirical relations between degradation (presented as loss of platinum area) and periodical voltage profiles have been proposed [5,6]. Kneer et al. [6] proposed a first order kinetic model, (4), (5), where S is the Pt surface area, N are the numer of cycles, and *k* is as factor composed of coefficients that depend on several operating conditions: k_{SC}, a baseline degradation, k_T, related to the temperature, k_{RH} related to the humidity and k_V related to the voltage profile, which is also composed of two features, upper voltage level, k_{UPL} and the time at upper level, k_{dwell}.

$$\frac{dS}{dN} = -kS(N) \tag{4}$$

$$k = k_{SC} * k_T * k_{RH} * k_V \,; \qquad k_V = k_{UPL} * k_{dwell} \tag{5}$$

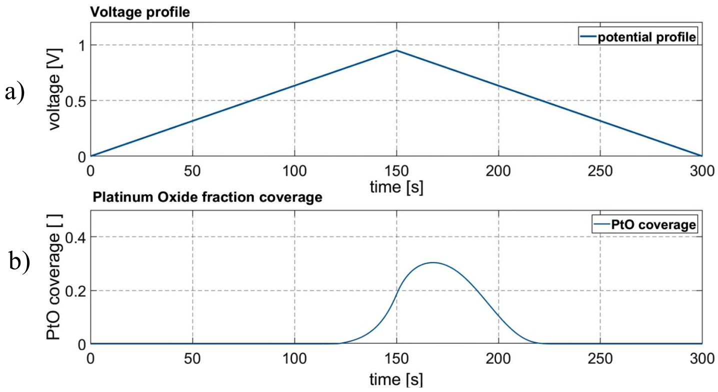

Figure 1. a) A sweep of increasing and decreasing voltage (triangular profile) is applied to our simulation model of Pt reaction kinetics. b) The result in fraction of Platinum Oxide (PtO) coverage.

Our objective is in trying to generalize the degradation-voltage profile relation and increase the number of voltage features to analyse, in order to define the most appropriate load (mission) profile to reduce the degradation of the PEMFC and improve control over its operating conditions.

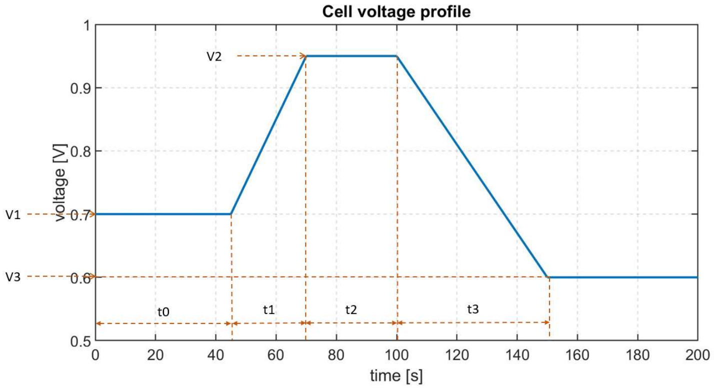

Figure 2. A generic voltage profile: one cycle is defined as a transition from three different levels of voltage, starting from a first voltage at time t0, passing through a different level at t1-t2 and reaching a final voltage at t3. Cycles have different voltages and transition times.

Figure 2 shows the proposed features to evaluate the load profile "quality" of a single cycle in terms of cell degradation. The degradation rate (long term cell voltage decay due to ECSA reduction) is assumed to be a function of this vector of features:

$V_1 = voltage\ level\ at\ time\ t_0$

$V_2 = voltage\ level\ at\ time\ t_2$

$V_3 = voltage\ level\ at\ time\ t_3$

$t_0 = time\ at\ V_1$

$t_1 = time\ of\ transition\ from\ V_1\ to\ V_2$

$t_2 = time\ at\ V_2$

$t_3 = time\ of\ transition\ from\ V_2\ to\ V_3$

3. Results and Discussion

3.1 Voltage wave with variable features

Figure 3 shows the features of 7 different testing voltage waves and the corresponding results in the evolution of PtO. The oxidation/reduction kinetics of platinum varies with the different characteristics of the voltage wave. Voltage levels, slew rates and cycling frequency at a scale of each cycle is important to determine better control and energy management strategies for improvement of PEMFC durability. Our future endeavour is to define an analytical expression to relate the vector of features to the degradation ratio and therefore "qualify" different mission profiles.

Voltage profile	Features							PtO Area
	V_1	V_2	V_3	t_0	t_1	t_2	t_3	
1	0.65	0.95	0.50	65	0	75	0	36.3
2	0.65	0.95	0.50	45	20	60	15	35.1
3	0.65	0.95	0.50	45	55	50	0	27.8
4	0.70	0.95	0.60	45	25	30	50	31.1
5	0.60	0.85	0.60	45	25	30	50	8.7
6	0.60	0.85	0.60	45	25	80	0	14.3
7	0.65	0.95	0.50	45	25	30	50	26.1

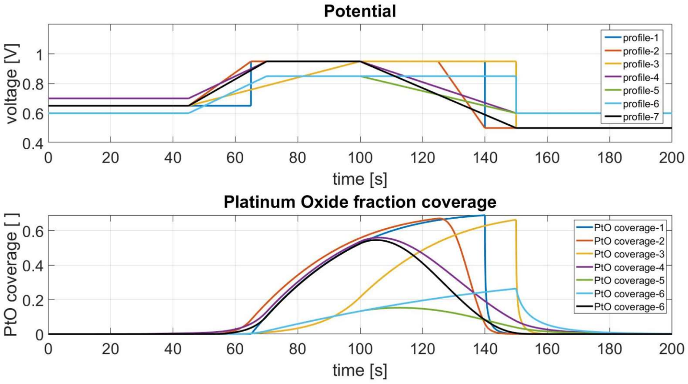

Figure 3. Seven different voltage profiles and the corresponding platinum oxide evolution, the area of the PtO coverage is related to the grade of degradation produced in the cell by the cycle of voltage.

4. Conclusions

Analysis of load profile and control strategies based on its definition, aiming at reduce the PEMFC degradation in the long term, are of interest to widen the usage of fuel cells as power plants by taking advantage of specific application characteristics. This scheme of control will help to extent the useful lifetime of fuel cells when used as power plant in vehicles with the capacity, to some extent, of deciding or forecasting the load profile of its future consumption by way of choosing from posible trayectories, velocities and accelerations within some constraints (figure 4); examples of such vehicles are, autonomous mobile equipments such as mobile robots used for research/exploration, or vehicles used in warehouse and factory intralogistics automation such as Autonomous Guided Vehicles (AGV) or robotic forklifts,

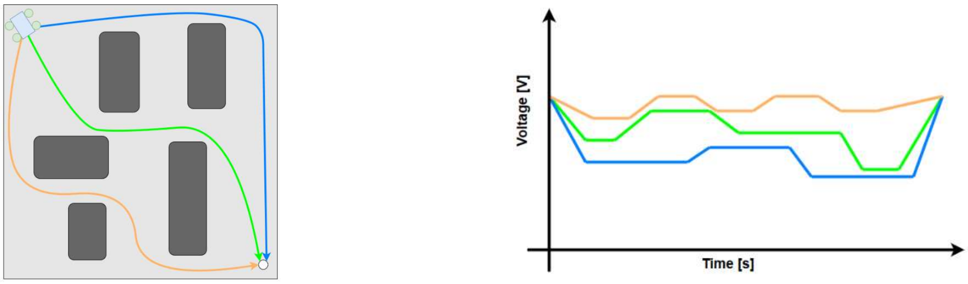

Figure 4. An autonomous mobile vehicle searches a navigation path taking into account the voltage profile that minimize catalyst degradation.

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