



Degradation Estimation of Polymer Electrolyte Fuel Cell under Different Cyclic Load Profiles

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ABSTRACT

Polymer electrolyte fuel cells (PEFC) find a suitable application in automotive vehicles as the prime mover. During its lifetime operation, a PEFC is subjected to various types of loading conditions, most of which are cyclic in nature. However, cyclic loading has been found to adversely affect the Pt catalyst cathode of a PEFC by dissolution and agglomeration of the Pt particles. It results in reduction of active electrochemical surface area, and hence reduced performance of the PEFC. In the present study, the degradation estimation of Pt catalyst cathode of a PEFC under various cyclic load profiles has been studied. Rectangular and trapezoidal load profiles have been selected with different duty cycles. The degradation estimation is based on the Pt agglomeration model, which can predict the electrochemical surface area (ECSA) at the end of set number of cycles. It was found that different voltage profile can affect the ECSA degradation in the PEFC. Degradation effect is evaluated based on the change in the electrochemical surface area, which renders to performance degradation. The Ostwald ripening effect for the Pt particles with operating time is also studied. It was concluded that Ostwald ripening lead to growth of Pt particles, which further inversely affect the ECSA and causes performance degradation.

Keywords: Cyclic loading, Degradation, Electrochemical surface area, Platinum catalyst, Polymer electrolyte fuel cells

1. INTRODUCTION

Fuel cell is an electrochemical device that directly converts chemical energy of the fuel into electrical energy. Consequently, the conversion efficiency of fuel cells is much higher than the thermal systems such as combustion engines. In addition to that fuel cells do not generate harmful emissions, hence they are considered future of the prime movers. Polymer electrolyte fuel cells (PEFC) are low temperature fuel cells, which offer high energy density and quick start-up characteristics, and hence ideal for automotive applications [1]. The fuel cell technology has advanced significantly in the recent years and has reached to the commercialisation stage. However, performance of fuel cell over its life time and hence reliability need further improvements. Therefore, estimation of

performance degradation with time is important for design and cost reduction of the system.

In PEFC, noble metals are used as electro-catalysts in the electrode materials to facilitate the chemical reactions. Platinum (Pt) is a commonly employed catalyst in the PEFC. Finely powdered Pt are dispersed over a carbon support to enhance the surface area at the cathode. It help in reduction of oxygen received from the atmosphere at the cathode. It has been found that small Pt particles tend to recombine into large particle over the time during operation of the PEFC [2-3]. This lead to reduction in active surface area of catalyst and hence reduced performance of the electrode. Therefore, higher Pt loading is required to improve the performance of the PEFC. It can be noted that Pt is a rare earth metal and hence it accounts for the major cost of a PEFC. Hence, for both performance as well as cost optimization of the PEFC, it is important to reduce the Pt loading as well as its degradation with time.

2. LITERATURE REVIEW AND OBJECTIVE

The deterioration of cathode catalyst could be caused by many simultaneous phenomena and hence it is difficult to model such a system. However, many research attempts have been made in this area in which, agglomeration of Pt catalyst is weighted most. This phenomenon is well known by Ostwald ripening effect, where smaller particles in solution dissolve and deposit on larger particles to minimize their surface energy and achieve a more stable state [4-5]. It has been reported that various parameters affect degradation of cathode catalyst such as operating temperature [6], cathode pressure [7], relative humidity [7], electrolyte PH and cell voltage [8-10]. It has been found that variation of cell voltage during the operation of a PEFC has detrimental impact. Therefore, many researchers has tried to capture this effect by studying the fuel cell performance under cyclic loading conditions. Uchimura et al. [10] studied the PEFC performance under simulated cyclic loading conditions between cell voltage ranges of 0.6 V to 0.95 V. Their study explains the effect of various operating parameter such as temperature and relative humidity of the PEFC under cyclic loading. Similarly, Mitsushima [9] studied the degradation of Pt cathode in PEFC under rectangular and triangular waves type

cyclic loading conditions. It was found that the Pt degradation rate could be increased by an order of ten if asymmetric triangular loading was used. Bezmalinovic et al. [11] reported that degradation of PEFC was due to increased resistance and activation losses when subjected to accelerated stress test conditions. Both of these effects can be linked to the loss of active catalyst surface area. Zang et al. [12] suggested different accelerated stress test protocols to study the cyclic loading conditions of PEFC. Selvaganesh et al. [13] studied the Pt-Au cathode degradation under accelerated stress test conditions. It was found that Pt-Au cathode degradation was 10% as compared to 60% for Pt cathode after 7000 cycles. The effect of mechanical vibrations on Pt cathode catalyst was studied by Diloyan et al. [14] under potential cyclic conditions. Under 300 hour accelerated stress test conditions, it was found that agglomeration of Pt particles are 10% less under mechanical vibration (20 Hz) than without vibration conditions. Similarly, simulated start-stop conditions of PEFC was studied by Meier et al. [15] on degradation of Pt catalyst cathode. The start-stop condition is one of the most severe cyclic conditions under which a PEFC is subjected in vehicular operating conditions.

The first step in the development of an improved cathode of PEFC is the accurate estimation of its performance degradation with time. A model based prediction mechanism of the performance of Pt based cathode with time is presented in this article. The major objective of this work is to study the degradation behaviour of Pt catalyst cathode PEFC with different loading cycles.

3. MATERIALS AND METHODS

In the present study, a catalyst layer modelling is used to evaluate the operating performance of PEMFC. The methodology used for the agglomerating modelling of the catalyst layer is based on the Ref. [16]. Agglomerate modelling provides the accurate FC behaviour as compared to the homogeneous and interface models [17].

The assumptions made in present study are given below:

- Hydrogen and oxygen gases are assumed ideal gases and pure.
- Steady state conditions are assumed for the modelling.
- The reactions are taking place at isothermal and isobaric conditions.
- Shape of agglomerate particles are assumed spherical and identical.
- It is assumed that GDL is filled with liquid water.

The governing equations for the modelling are given as below:

Electrochemical reaction rate can be formulated as given below [17]:

$$\frac{di}{dz} = 4F \frac{P_{O_2}}{H_{O_2,i}} \left(\frac{1}{E_r k_c (1 - \varepsilon_{CL})} + \frac{(r_{agg} + \delta_{agg}) \delta_{agg}}{a_{agg} r_{agg} D_{O_2,i}} \right)^{-1} \quad (1)$$

where i denotes current density and z represents the cathode layer thickness. r_{agg} and δ_{agg} are radius and thickness, respectively of agglomerate particles.

In Eq. (1), the second term captures the effect of the agglomerate modelling on the PEFC performance. Diffusion of

oxygen and oxygen concentration gradient can be represented as below [17]:

$$\frac{dC_{O_2}}{dz} = \frac{i - I_{tot}}{4FD_{O_2,CL}} \quad (2)$$

where C_{O_2} is concentration of oxygen at cathode layer.

The relation between the resistances and the activation overpotential can be given by the following expression as [17]:

$$\frac{d\eta_{act}}{dz} = \frac{i}{k_{eff}} + \frac{i - I_{tot}}{\sigma_{eff}} \quad (3)$$

where η_{act} is activation overpotential. k_{eff} and σ_{eff} are bulk effective protonic conductivity and bulk effective electronic conductivity, respectively.

The Eqs. (1), (2) and (3) require three boundary conditions to solve them.

Boundary condition 1: The concentration of oxygen at the CL/GDL ($z=0$) interface, can be expressed by Henry's law as follows [18]:

$$(C_{O_2})_{z=0} = \frac{P_{O_2}}{H_{O_2,w}} \quad (4)$$

where Henry's constant for oxygen in water can be found out using the expression:

$$H_{O_2,w} = 1.33 \times \exp\left(\frac{-666}{T}\right) \quad (5)$$

Boundary condition 2: All the protons which travel from the anode side to the cathode catalyst layer are assumed to be consumed before they reach the CL/GDL boundary. Therefore:

$$(i)_{z=0} = 0 \quad (6)$$

Boundary condition 3: The protonic current density attains its final value at the CL/Mem interface, thus:

$$(i)_{z=L_{CL}} = I_{tot} \quad (7)$$

The physical significance and detailed information of all terms are provided in the Ref. [16]. It is worth to be mentioned that the effect of Ostwald ripening effect in the second term (Eq.1) is not considered in present study.

Some primary results of the modeling are shown in Fig.1, Fig.2 and Fig.3. The variation in the current density along with the catalyst layer is shown in Figure 1. Figure 2 shows maximum oxygen is consumed near the catalyst layer and GDL interface. The variation in the activation overpotential is shown in Figure. 3.

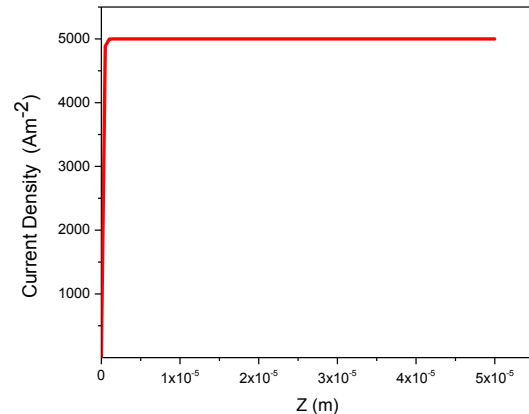


Figure 1: Variation of the current density with catalyst layer.

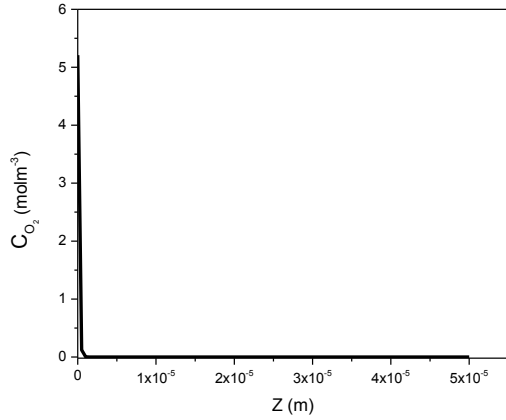


Figure 2: Variation of the oxygen concentration with catalyst layer.

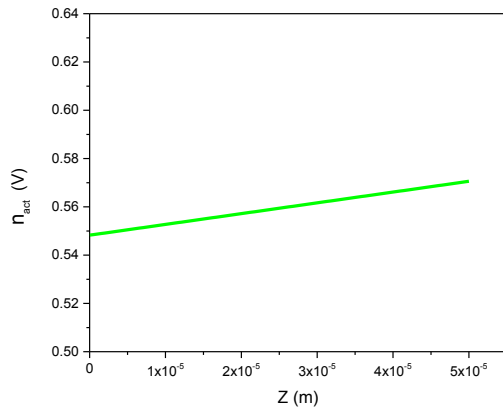


Figure 3: Variation of the activation over-potential with catalyst layer.

The change in the electrochemical surface area (ECSA) is subjected to the various parameters i.e. temperature, relative humidity and cyclic loading.

One can normalize the value of ECSA as follows:

$$S_N = \frac{(ECSA)_N}{(ECSA)_{N=0}} \quad (8)$$

A limit for the number of cycles N can be defined after that ECSA remains stable at minimum value. This means $S_{min} = S_{N>N_e}$, S_{min} is defined as follows:

$$S_{min} = \frac{(ECSA)_{min}}{(ECSA)_{N=0}} \quad (9)$$

The expression for S_N in terms of number of cycles and S_{min} is as follows:

$$S_N = S_{min} + (1 - S_{min}) \times \exp(-KN) \quad (10)$$

Therefore, α indicating factor is defined to represent the S with numbers of cycles.

$$\alpha = (S - S_{min}) / (1 - S_{min}) \quad (11)$$

In this study, different cyclic load profiles are considered to evaluate the effect of cyclic loads on the FC degradation. Fig. 4 represents the different cyclic loads.

The symbol L1, L2, L3, L4, L5, L6 are used for the different load profiles.

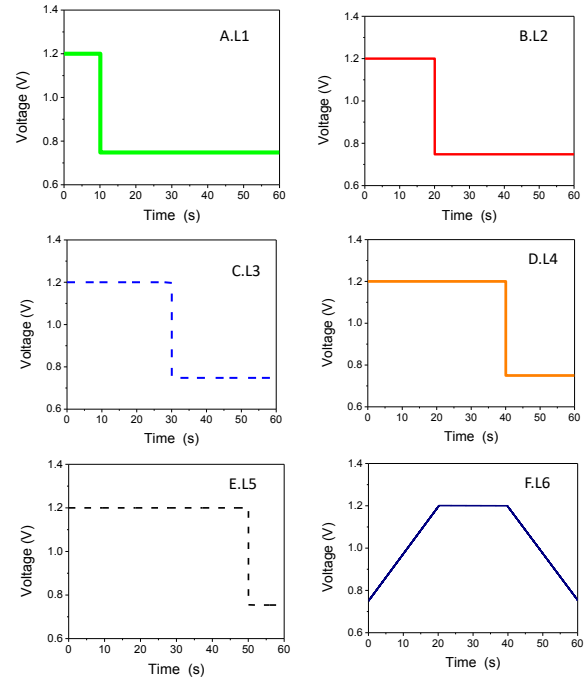


Figure 4: Details of various load profiles used the present study.

The proportionality constant K is defined as:

$$K = K_{SC} \times K_T \times K_{RH} \times K_V \quad (12)$$

where K_{SC} , K_T and K_{RH} are proportionality constants for standard conditions, temperature correction factor, relative humidity correction factor and cyclic load protocol correction factor.

Thus, one can write using the proportionality in the expression (12):

$$\frac{K}{K_{SC}} = \frac{V_{amp}}{(V_{amp})_{SC}} \times \frac{\exp(V_{ave})}{\exp((V_{ave})_{SC})} \times \frac{\Delta t}{(\Delta t)_{SC}} \quad (13)$$

where, standard test conditions are given as below:

Operating temperature = 60° C

Relative humidity=100%

Load profile – Square shape load profile

Maximum voltage, V_{max} =1.2 V

Minimum voltage, V_{min} = 0.6 V

Time period, Δt = 60 s

Thus, considering the standard conditions cyclic load protocol correction factor can be written as below:

$$K_V = \frac{V_{amp}}{0.6} \times \exp(V_{ave} - 0.9) \times \frac{\Delta t}{60} \quad (14)$$

Table 1: Values of parameters used in the study under base case condition [16]

Parameters	Value
Mass loading of platinum m_{Pt} (kg m ⁻²)	0.005
Mass loading of carbon m_C (kg m ⁻²)	0.045
Platinum density ρ_{Pt} (kg m ⁻³)	21400
Current density I_{tot} (A m ⁻²)	8000
Mole fraction of oxygen X_{O_2} (%)	21
Mole fraction of hydrogen X_{H_2} (%)	100%
Catalyst layer thickness L_{CL} (m)	5×10^{-5}
(ECSA) _{N=0} (m ² kg ⁻¹)	72000
Volume fraction of GDL in CL L_{GDL}	0.1
Ohmic resistance R_{ohmic} (Ω m ²)	7.2×10^{-6}
Carbon density ρ_C (kg m ⁻³)	1800
$C_{O_2}^{ref}$ (mol m ⁻³)	1.2
σ (Ω^{-1} m ⁻¹)	$72700 \Omega^{-1}$
Initial radius of agglomerate particles $r_{0,agg}$ (m)	3×10^{-7}
δ_{agg} (m)	4×10^{-8}
Initial radius of platinum particles $R_{0,Pt}$ (m)	3.3×10^{-9}
Temperature T (°C)	80
Pressure P (atm)	5
Relative humidity RH (%)	100
γ_{Pt} (J m ⁻²)	2.37
Pt molar fraction Ω_{Pt} (m ³ mol ⁻¹)	9.09×10^{-6}
Constant during standard conditions K_{SC}	4.537×10^{-4}

Cyclic loading condition causes the Ostwald ripening of the agglomerate particles at the cathode catalyst layer. During Ostwald ripening the Pt particles dissolve in the ionomer phase where they aggregate together and makes bigger particles. During this process the average size of Pt particles grows. If the size of the Pt particles is larger than the critical size, then particles start coarsening and larger particle swallow smaller one. Thus, the mean radius of the particles increases, and their numbers decrease.

The expression of the difference of the cubes of the initial and final radius of the platinum particles is as follows:

$$R_{t,Pt}^3 - R_{0,Pt}^3 = \frac{8D_{Pt,N}\Omega_{Pt}^2 C_{\infty,Pt} \gamma_{Pt} t}{9RT} = k_d t \quad (15)$$

Thus:

$$k_d = \frac{8D_{Pt,N}\Omega_{Pt}^2 C_{\infty,Pt} \gamma_{Pt}}{9RT} \quad (16)$$

From equations (15) and (16) the expression for the mean radius of agglomerate particles at any time is as follows:

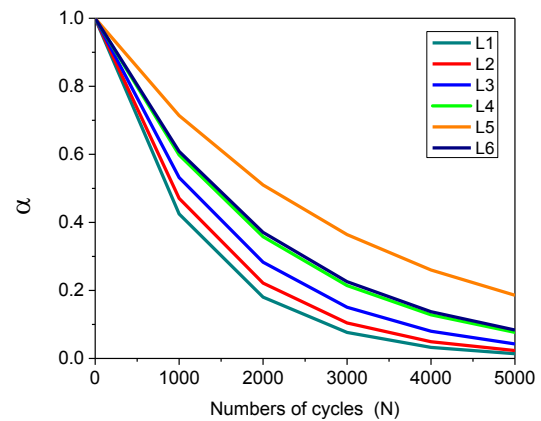
$$r_{agg} = r_{0,agg} \times \sqrt[3]{1 + \frac{k_d t}{R_{0,Pt}^3}} \quad (17)$$

4. RESULTS AND DISCUSSION

The variation in the ECSA with increase in the numbers of cycles is represented in the Fig.5. It was found that ECSA decreased with increase in the number of cycles. A decrease in ECSA can lead to the performance degradation in the FC with numbers of cycles (operating time) as it will decrease in the electrochemical reaction rate. It is worth to mention that operating temperature (80 °C) and relative humidity (RH=100%) are considered same in all the cases. The different operating conditions such as temperature and relative humidity can lead to different ECSA degradation (refer Eq. (9)).

The rate of ECSA degradation was found higher for the load profile L1. It is because the cyclic load protocol correction factor depends on the average value of the load which is minimum for the L1 profile (Eq. (14)). This leads to higher declination in the ECSA (Eq. (10)). While ECSA degradation rate is found to be minimum for the load profile L5 as average value of the load voltage is higher in this case as compared to the others load profiles.

Fig. 6 represents the variation in the indicating factor, α along with the given numbers of cycles (refer Eq.10). It was found that α decreased with increase in the numbers of cycles. This decrease in the α can describe a degradation in the FC with numbers of cyclic loads. However, more severe degradation is found with load profile L1. The trend in the degradation of indicating factor α can be explained as similar to the ECSA degradation which has been already discussed.

**Figure 5: Variation of the normalized ECSA factor with the number of cycles.**

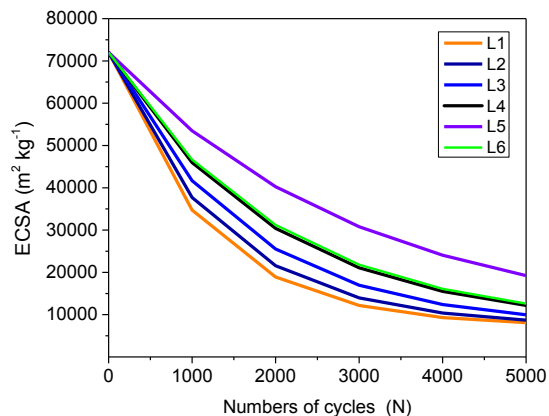


Figure 6: Variation of the ECSA with the number of cycles.

Table 2: Ostwald ripening of Pt particles (T=80 °C, load profile L2, RH=100%)

Number of cycles N	5000 (60 s×5000=300000 s)
ECSA (kg m ⁻²)	8.70×10 ³
C _∞ (mol m ³)	8.75×10 ⁻⁸
K _d (m ³ s ⁻¹)	5.19×10 ⁻³¹
R _i (m)	5.72×10 ⁻⁹
r _i (m)	5.24×10 ⁻⁷
α	2.31×10 ⁻²

The Table 2 shows ostwald ripening behaviour in the FC with time. The Ostwald ripening cause a rise in the agglomerate particles with an increase in the numbers of cycles as shown in Table 2. The radius of the Pt particles increases from 3.3×10^{-9} m to 5.72×10^{-9} m with operating time due to Ostwald ripening effect. The other parameters for formulation of Ostwald ripening effect are also provided in Table 2. The effect of growth of size of Pt particle can be interpreted as performance degradation in FC. The ECSA is proportional to the outer surface area of Pt particles (areas per unit mass). This area is inversely proportional to the radius of the Pt particles. Therefore, as size of the particles grows with time, the ECSA will decline which renders less electrochemical reaction rate.

5. CONCLUSIONS

Present study shows the degradation in the PEFC with operating time for different cyclic load profiles. It was found that different voltage profile can affect the ECSA degradation in the PEFC. The load profile L1 showed the highest degradation amongst the various profiles studied. Degradation

effect is evaluated based on the change in the ECSA, which renders to performance degradation. The Ostwald ripening effect for the Pt particles with operating time is also studied. It is concluded that Ostwald ripening leads to growth of Pt particles, which further inversely affect the ECSA and causes performance degradation. A study can be performed in the future to evaluate the effect of the ECSA variation with the operating time on the fuel cell output performance such as voltage degradation.

ACKNOWLEDGEMENTS

We would like to acknowledge the support of Birla Institute of Technology and Science, Pilani campus, Pilani (BITS Pilani) under Additional Competitive Research grant (ACRG) to support the present work.

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