



## The Analysis on the Activation Procedure of Polymer Electrolyte Fuel Cells

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### ABSTRACT :

It is, in general, believed that during the activation process, the proton conductivity increases due to wetting effect and the electrochemical resistance reduction, resulting in an increase in the fuel cell performance with time. However, until now, very scant information is available on the understanding of activation processes. In this study, dominant variables that effect on the performance increase of membrane electrode assemblies (MEAs) during the activation process were investigated. Wetting, pore restructuring and active metal utilization were analyzed systematically. Unexpectedly, the changes for both ohmic and reaction resistance characterized by the electrochemical impedance spectroscopy (EIS) after initial wetting process were much smaller when considering the degree of cell performance increases. However, the EIS spectra represents that the pore opening of electrode turns into gas transportable structure more easily. The increase in the performance with activation cycles was also investigated in a view of active metals. Though the particle size was grown, the number of effective active sites might be exposed more. The impurity removal and catalytic activity enhancement measured by cyclic voltammetry (CV) could be a strong evident. The results and analysis revealed that, not merely wetting of membrane but also restructuring of electrode and catalytic activity increase are important factors for the fast and efficient activation of the polymer electrolyte fuel cells.

**Keywords:** Polymer electrolyte fuel cells, Activation, Electrode, Impurities, Structure

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### 1. Introduction

Polymer electrolyte fuel cells (PEFCs) are promising energy conversion system for automotive, mobile and stationary applications because of their low operating temperature, fast startup and high power density.<sup>1)</sup> The PEFC is comprised of an electrolyte with high ionic conductivity, two porous electrodes (anode and cathode) with electro-catalysts and gas diffusion layer (GDL) on each side.<sup>2)</sup> The membrane electrode assembly (MEA) is

the main parts for the generating electricity in PEFCs. The hydrogen oxidation reaction (HOR) and the oxygen reduction reaction (ORR) take place at the anode and cathode, respectively. In addition, the oxidation and the reduction reactions can only occur at specific sites called triple phase boundaries constituted by electrolyte, gas, and catalyst regions. Particularly, the oxygen reduction reactions are the major issue, since a slow reaction rate significantly limit the overall fuel cell reaction kinetics, resulting in considerable performance loss.<sup>3,4)</sup>

To get, in general, the maximum performance of the PEFC systems, activation process or wetting process is known as an essential procedure. The newly assembled

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cell and stack should be experienced certain voltage cycling procedure to increase the performance. For the activation process, fuels, stack operation system, labor, time, etc. are necessary. On the other hand, the cost of activation process needs to be minimized from industrial point of view. Though, until now, the PEFC research has long history, it's not clearly understood on the activation process yet. There is restricted number of reports on the activation of PEFCs. Unstable performance before the cell activation seems due to following facts: (i) Reactant cannot be supplied to the catalyst active sites properly due to some blockage, (ii) Lack of hydration of Nafion around the catalyst and (iii) an ionic conductivity disconnection between catalyst layer and membrane.<sup>5)</sup>

In the present study, the dominant factors for the performance increase during activation process were investigated. We endeavored to inspect the effect of wetting, electrocatalytic activity and electrode structural change, separately. Systematic electrochemical analyses were conducted for the commercially available MEAs and the phenomena in MEAs during activation process were suggested in schematic.

## 2. Experimental

Single cell used in this investigation is assembled using a commercial MEA (Reinforced membrane) with an active area of 50 cm<sup>2</sup>, a pair of gas diffusion layer (Sigracet 10 BC : SGL carbon Inc.), and bipolar plate with serpentine graphite flow fields. Reactant gases control and cell performance evaluation were conducted by a fuel cell test station which is designed and manufactured in-house. Fully humidified hydrogen and air were supplied to the anode and cathode, respectively. The stoichiometric ratio was set as 1.5 for hydrogen and 2.0 for air. The activation procedure used in this study is shown in the Fig. 1. To investigate the kinetics(charge transfer) and the ohmic resistance, electrochemical impedance spectroscopy (EIS) was conducted by an ac-impedance system with constant-current mode 1A(20 mA/cm<sup>2</sup>), sweeping frequency range of 100 kHz-100 mHz and an amplitude of 30 mA with 10 points/decade using an EIS potentiostat (Bio-Logic Science Instruments, HCP-803). In order to inspect the variations of electrochemical characteristics during the activation process, cyclic voltammetry(CV) was performed from 0.01 V-1.2 V at a scan rate of 50 mV/s. Fully humidified hydrogen and nitrogen with 371 ml/min and 1326 ml/min, respectively, at 70 °C were supplied to the anode and cathode.

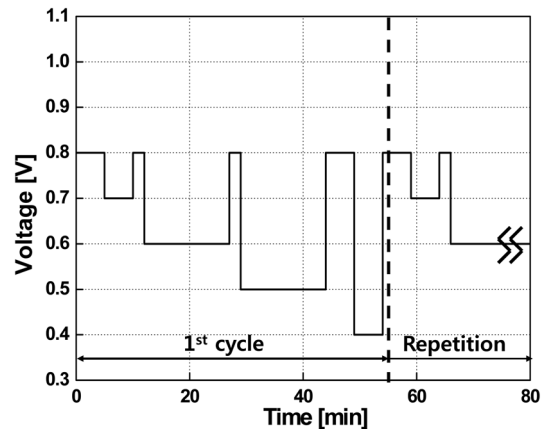


Fig. 1. A general activation procedure for MEAs by voltage cycling.

## 3. Results and discussion

### 3.1. Wetting effects on the cell performance during activation procedure.

The wetting of electrolyte in PEFCs has been thought as the most important factor during the activation process. The increase of proton conductivity in the membrane and the ionomer by wetting was believed as a dominant factor of cell performance rise. In the fuel cell system, without mass transport limitation, fuel cell performance is given by following equation (1):

$$V = V_0 - (b \log I) - RI \quad (1)$$

Where  $V$  is the cell voltage in mV,  $V_0$  the cell voltage at minimal current densities, which can be taken as the open circuit voltage(OCV, mV),  $b$  the Tafel slope in mV/decade,  $R$  the cell resistance in  $m\Omega \cdot cm^2$  and  $I$  is the current density in  $mA/cm^2$ . Performance of the fuel cell can be increased by means of both improving the ionic conductivity and reducing the total cell resistance. In the steam treatment procedure of the fuel cell, as indicated Fig. 2, the total cell resistance decreases due to the hydration effect. About 90% of total cell resistance markedly decreased just in fifteen minutes and then gradually declined to 72  $m\Omega \cdot cm^2$  at the steaming time of 20 h. Based on this result, it can be inferred that wetting it self of the cell was almost completed within fifteen minutes. Fig. 3 shows the performance increase with the number of activation cycle. The performance reached to the maximum value at the 8<sup>th</sup> cycle and then stabilized. The relationship

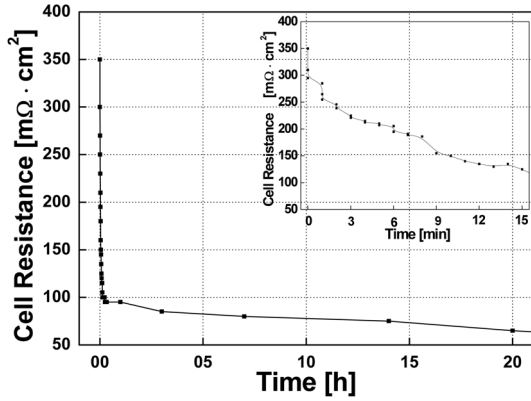


Fig. 2. Change in cell resistance during mere hydration treatment.

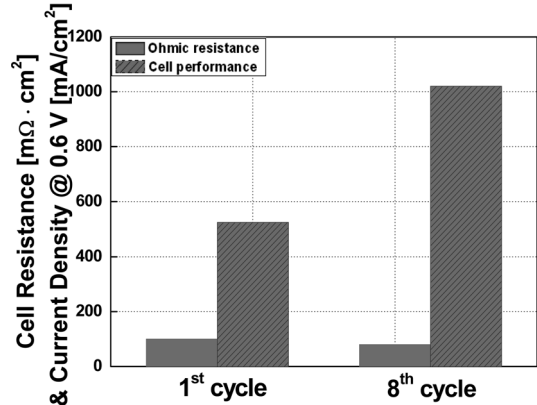


Fig. 4. Comparison of changes in the ohmic resistance and the cell performance during the activation procedure.

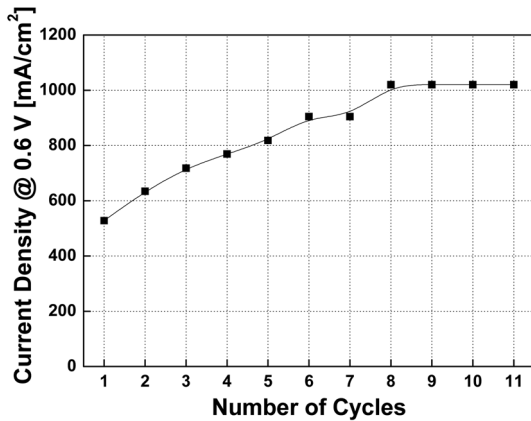
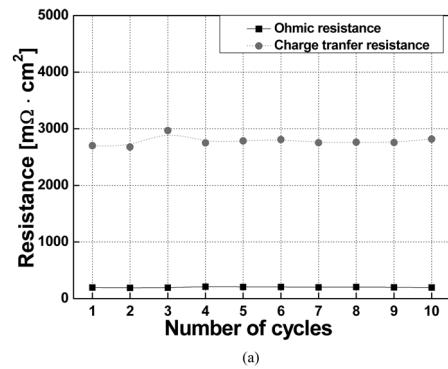
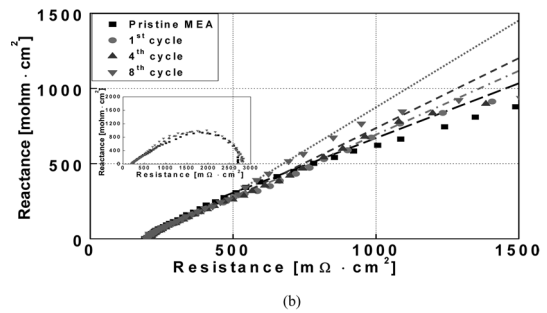


Fig. 3. Performance increase of MEA during activation procedure.



(a)



(b)

Fig. 5. Plots of electrochemical impedance spectroscopy with activation cycles.(a) Changes in the ohmic and the charge transfer resistances, (b) changes in the slope at high frequency arc of Nyquist plot.

between the ohmic resistance and the performance of the cell is summarized at Fig. 4. The cell performance increased dramatically during activation process, but the degree of the cell resistance changes was not noticeable. Depending on the above results, it's difficult to find a direct correlation between increased cell performance and ohmic resistance. There should be other critical factors that affect on the performance enhancing during the activation procedure.

### 3.2. Changes in pore structure of electrodes during activation procedure

To better understand the cell performance changes during the activation procedure, electrochemical impedance spectroscopy(EIS) measurements carried out under ac-impedance system at constant-current mode

1A(20 mA/cm<sup>2</sup>) as shown in Fig. 5. In the PEFCs system, the ohmic resistance is comprised of the membrane, catalyst layer, GDL, plates and the contacting interfaces of cell components. The charge transfer resistance usually shows the characteristics of the cathode, which consists

of two arcs. The higher frequency arc reflects charge transfer resistance and the lower frequency resistance reflects mass transfer limitations.<sup>6)</sup> As shown in Fig. 5(a), both of the ohmic and charge transfer resistance changes with activation cycles were negligible. It also supports the result of Fig. 4, i.e. some other critical factors affecting on the performance during the activation procedure could be exist. Fig. 5(b) represents the Nyquist plot during the activation procedure. At high frequency arc, the slope changed more steeper with cycles (from 26.5° to 44.4°). It can be analyzed that the entrance of pores in the electrode was opened largely during activation procedure. Thus, this phenomenon affects that the reactant easily access catalytic sites in the electrode. The relationship between pore characteristics and EIS results is depicted at Fig. 6.<sup>7)</sup> At high frequency arc, the slope is steeper at the pores with wide entrance relatively at Fig. 6. It can be one of the direct evidence of for improved utilization of active sites on metal particles with the number of activation cycle. Therefore, the structural changes in the electrodes by the rearrangement of catalyst, pore size, pore shape and tortuosity increased the reactant accessibility and cell performance.

### 3.3. Changes in active metal characteristics during activation procedure

The properties of the active metal (mainly Pt) of the electro-catalyst were investigated in two categories. One is the morphological aspect and the other is the impurity aspect. In Fig. 7, three typical cyclic voltammograms (CVs) for (i) pristine MEA, (ii) just hydrated

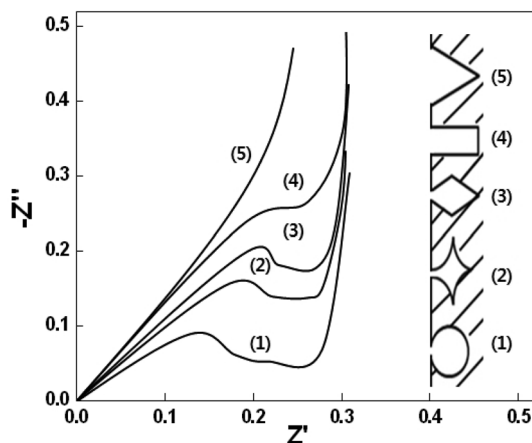


Fig. 6. Schematic diagram of the electrochemical impedance spectroscopy (EIS) according to the pore structure (Reproduced from<sup>7)</sup>).

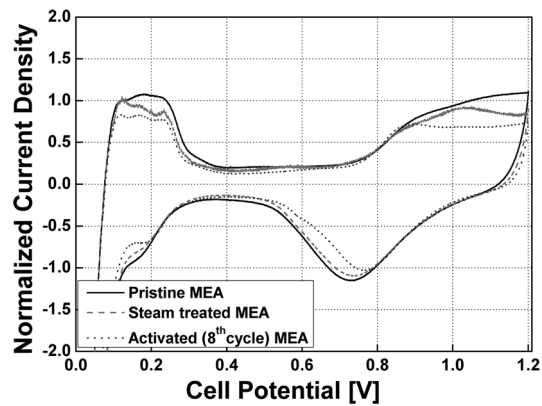


Fig. 7. Cyclic voltammograms (CVs) for the MEAs with the activation step.

MEA and (iii) activated (8<sup>th</sup> cycle) MEA given, respectively. As the activation cycles progress, the hydrogen desorption peaks around 0.2 V decreased. This can be interpreted to the decrease of Pt surface area, i.e. agglomeration of Pt particles. The phenomenon disagrees with the performance enhancement of cell during activation process. Though the electro-chemical surface area (ECSA) of Pt decreased, the on-set voltage of Pt oxidation lowered clearly with the activation cycles. The lowered on-set voltage means easier electrochemical reaction on the Pt surface. The on-set voltage changes expressed at Fig. 8 is a  $V$  at  $(I_{max} + I_{min})/2$ . The above results showed that, although, the Pt particles enlargement causing reduction of ECSA, the more active sites could be exposed to the reactants.

Besides the morphological changes of Pt particles during activation procedure, Pt poisoning related phenomena were observed in the CVs in Fig. 7. The CVs at

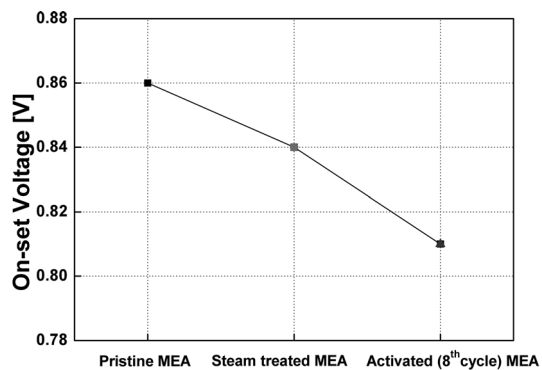
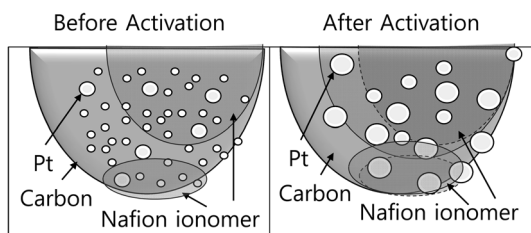


Fig. 8. Change of the on-set voltage ( $V$  at  $(I_{max} + I_{min})/2$ ) for for the MEAs with the activation step.



**Fig. 9.** Conceptual model for the morphological changes in the electrode during the activation procedure.

the voltage range from 0.8 V to 1.2 V definitely show gradual desorption of some kind of impurities mainly might come from the MEA fabrication process. After 9<sup>th</sup> cycle of activation procedure, impurities existed at the surface of Pt were almost removed. Moreover, just steaming process on the MEA also affected on the removal of impurities on the Pt surface. In the aspect of active metal, increase of catalyst activity and removal of adsorbed impurities could be directly correlated with the performance enhancement with activation cycles.

The schematics of the changes in the typical electrodes during activation procedure were depicted at Fig. 9. The pristine MEA may have much smaller Pt particles which might have low catalytic activity. During the activation process the Pt particles agglomerate to the moderate size exposing more number of active sites as well as effective three-phase interfaces, which can be explained by CV analysis. In addition, the Nafion ionomers swell nearly 22 vol% due to water absorption about 7 wt% within the electrode,<sup>8)</sup> which may also affect on the connectivity of proton transport path ways as well as structural changes. The simplified morphology of the activated electrode could be suggested in Fig. 9.

#### 4. Conclusions

To elucidate the critical factors increasing the cell performance during the activation procedure of PEFCs, commercially available MEAs were systematically analyzed. As the number of activation cycle increased, cell performance also dramatically enhanced till getting steady-state status. Until now, most of the researchers have believed

that a wetting of electrolyte during operation is one of the most important factors for the cell activations. However, it was difficult to find direct correlations between the performance changes and the ohmic and the charge transfer resistances, at least after initial wetting. In spite the ECSA of Pt decreased with the cycle, the cell performance showed a big increase. It could be explained by the three supporting results; pore-openings, catalytically active sites and desorption of impurities. The EIS showed the possible pore opening phenomena in the electrode, which enhance the reactants mobility. The on-set voltages and the impurities on the Pt surface were clearly decreased with the number of activation cycle. The catalytic activity issue rather than the electrolyte wetting issue may be the much critical factor in the activation procedure in polymer electrolyte fuel cells. Based on the results, more efficient activation processes can be suggested for both industries and research groups.

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