

Short communication

Activation of low temperature PEM fuel cells

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Abstract

Proton-exchange membrane (PEM) fuel cells intended to be operated at ambient conditions for portable applications are first activated by being exposed at elevated temperature and pressure. The performance of the resulting fuel cells, especially those whose electrodes are of low catalyst loadings made using supported catalysts, improve dramatically. The activation procedure is effective, quick and easy to perform. © 2002 Elsevier Science B.V. All rights reserved.

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The performance of a proton-exchange membrane (PEM) fuel cell is largely determined by the membrane-electrode assembly (MEA), which is composed of an anode for the fuel oxidation, a cathode for oxygen reduction, and an ion-conducting membrane for proton transportation. Since the fuel oxidation reaction and the oxygen reduction reaction are kinetically slow, noble metal catalysts such as platinum and its alloys are used to catalyze these reactions.

In order to reduce the cost of a fuel cell, one approach is to reduce the amount of catalysts used in the catalyst layers. Metal black with lower surface area was initially used. The catalyst loading in such electrodes needed to be over 4.0 mg/cm². Later on, much smaller metal nano-particles with higher surface area prepared onto a carbon support were used.

Since both electrons and protons are involved in fuel cell reactions, electrical as well as proton conductivities are needed. Traditionally, the reaction zone was limited within the interface between the catalyst layer and the ion-conducting membrane because the catalyst layer itself did not conduct protons. Since this interfacial region was extremely thin, the total surface area of the catalyst particles in this region was low, and thus the catalyst layer could not provide a very high current density. The catalyst that was not in contact with the membrane was simply wasted. This situation was changed when an ionic conductor such as Nafion was incorporated into the catalyst layers [1–10]. After Nafion incorporation, the entire catalyst layer conducts both

electrons and protons, so, the catalyst utilization in the layer is improved greatly.

All these recent achievements have helped to decrease the catalyst loading from 4.0 mg/cm² or higher to 0.5 mg/cm² or less. However, a fuel cell that uses low catalyst loading electrodes and operates under ambient conditions as portable power source, normally shows much lower performance than a fuel cell using higher catalyst loading electrodes. It seems that many catalyst particles cannot participate in reactions under such mild conditions [11].

This paper provides an effective and fast activation procedure to overcome this problem. The procedure not only is much shorter than a traditional “break-in” process but also increases catalyst utilization dramatically, especially for the electrodes with low catalyst loadings made using supported catalysts.

1. Experimental

Catalyst mixtures were prepared by directly mixing supported catalysts with Nafion solution. The mixture was stirred thoroughly before it was applied onto a gas diffusion medium such as ELAT and carbon paper. The electrodes were dried in an oven at 135 °C for 30 min, and then were hot-bonded onto Nafion 112 membranes at 130 °C for 3 min.

Single cell tests were carried out using a 10 cm² active area test fixture. The test fixture was composed of a pair of metal plates with serpentine flow-fields. The plates were coated with metal nitride for corrosion protection. Rod-like heaters were inserted into the plates to control the cell temperature. Air and pure hydrogen were used as the

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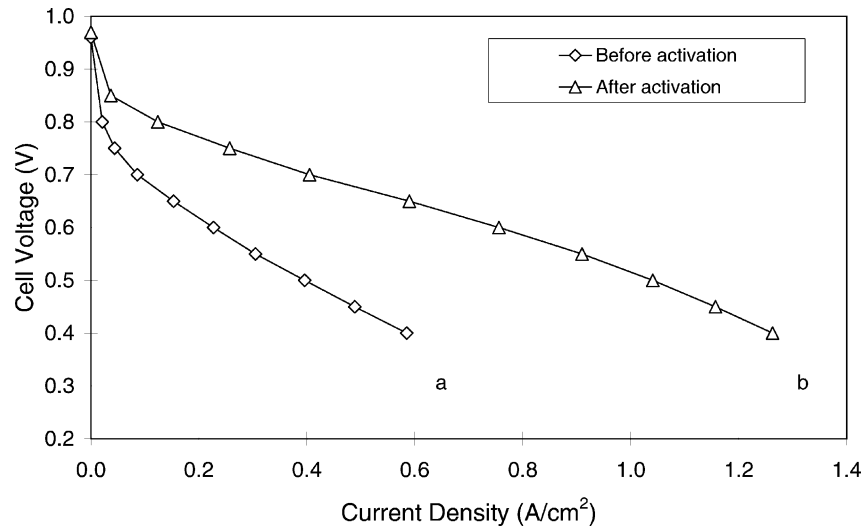


Fig. 1. Performances of a cell (a) before and (b) after a 120 min activation. $T_{\text{cell}} = 35^{\circ}\text{C}$, $T_{\text{humidification}} = 45^{\circ}\text{C}$, Nafion 112 membrane, Pt = 0.12 mg/cm².

reactants. If the gas needed to be humidified, it was passed through a stainless steel water bottle; otherwise, the gas bypassed the humidifier and entered the cell at room temperature. A cell temperature of 35 °C, hydrogen inlet temperature of 45 °C, and air inlet temperature of 45 °C is denoted herein as 35/45/45 °C. The stoichiometries of air and hydrogen were controlled using flow meters to about 10 at a current density of 2.0 A/cm². The load was varied using a rheostat when voltage (V)–current density (I) curves were collected.

2. Results and discussion

Fig. 1 shows the performance of a cell using electrodes with a Pt loading of 0.12 mg/cm² made from E-TEK 20% Pt/Vulcan XC-72 before and after an activation procedure.

Curve (a) shows the performance before the activation but after the cell had been operated at 35/45/45 °C for 180 min. During this time period, the performance increased gradually, but after 180 min, the cell did not show apparent further increase. The cell seemed to have reached its highest performance no matter how much longer it would be run under this condition. An activation was then carried out at a cell temperature of 75 °C, hydrogen humidification temperature of 95 °C, air humidification temperature of 90 °C, hydrogen backpressure of 20 psig, and air backpressure of 30 psig. We denote such an activation condition as 75/95/90 °C and 20/30 psig hereinafter. During the activation, the cell voltage was set at 0.40–0.60 V for most of the time to sustain a current density of 1.0–1.5 A/cm², but periodically the load was adjusted in such a way that the cell voltage was changed from open circuit voltage to as low as 0 V. The cell performance at 75/95/90 °C and 20/30 psig was recorded

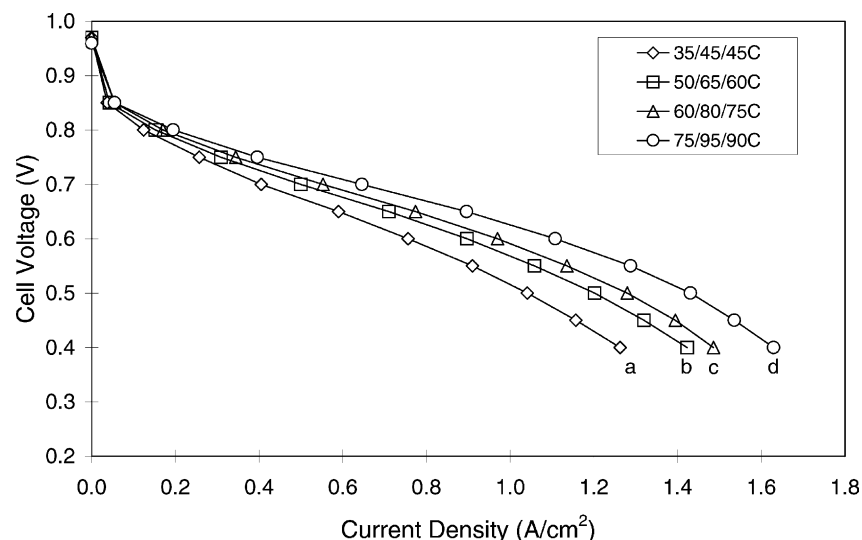


Fig. 2. Performances of an activated cell at different temperatures. Nafion 112 membrane, Pt = 0.12 mg/cm².

periodically until it did not show any further increase. The temperatures of the cell and the humidifiers were then decreased to 35 and 45 °C, respectively. Curve (b) shows the performance of the same electrode but after a 120 min activation. A dramatic increase in performance was achieved. For example, at a cell voltage of 0.50 V, the current density was increased from 0.40 to 1.04 A/cm². Such an increase could never be achieved if the cell were only tested at 35/45/45 °C.

Fig. 2 shows the performance of the activated electrode at different cell and humidification temperatures. The conditions for Curves (a–d) were 35/45/45, 50/65/60, 60/80/75 and 75/95/90 °C, respectively. The humidification temperature was increased as the cell temperature was increased to make sure that the MEA was fully hydrated. Although the reactants concentration or partial pressure decreased with increase of humidification temperature due to the presence of more water vapor, the cell performance increased with the cell temperature. Evidently, the increase in the kinetics of both oxygen reduction reaction and hydrogen oxidation reaction with temperature overcame the decrease in the reactants concentrations.

The activation effect was proved to be long-lasting. The activated electrode shown in Fig. 1 was tested for about 4 weeks. During this time period, the cell was either operated continuously for a few days, or shut down for one or several days then started next day, and at one time, the cell was frozen at –17 °C for 3 days. Curves (a and b) in Fig. 3 show the cell current densities at 0.70 and 0.50 V, respectively, when the cell was tested at 35/45/45 °C. The performance fluctuated slightly but the trend showed very little decrease in 4 weeks. It was believed that the fluctuation was due to water management rather than loss of activation. After the cell was frozen at –17 °C, it was difficult to start the cell because the passes for the reactants flow were blocked by

Table 1
Cell current density during an activation process

Cell current density (A/cm ²) at	Activation time (min)				
	5	30	60	90	120
0.40 V	1.295	1.344	1.380	1.384	1.370
0.70 V	0.508	0.568	0.603	0.652	0.654

ice. But once the ice was melted by the gaseous reactants, the cell gained good performance immediately.

The activation could be achieved extremely fast. Table 1 shows performance of a cell at 0.4 and 0.7 V, respectively during an activation process at 75/95/90 °C and 15/20 psig. The electrode had a Pt loading of 0.17 mg/cm² made using an old batch of Engelhard 20% Pt/C. The cell achieved 78% activation at 0.70 V and 93% activation at 0.40 V after as short as 5 min. After 30 min, the cell achieved 87% activation at 0.70 V and 97% activation at 0.40 V. After 60 min, the cell achieved 93% activation at 0.70 V and 100% activation at 0.40 V. After 90 min, the cell achieved 100% activation at 0.70 V too. Clearly, the activation proceeded very fast, and most of the activation was achieved in the first few minutes.

A variety of supported catalysts manufactured by different companies have been tested. They can all be fully activated within several hours although different catalysts may need different activation times. Generally speaking, the improvement in performance after activation is greater for catalysts with lower Pt contents on the support. The activation procedure is also applicable to electrodes made using unsupported catalysts such as Pt black, but the increase in performance is normally less than that of electrodes made using supported catalysts. The activation proceeds faster at higher cell temperature and higher gas backpressure. MEAs consisting of different kinds of membranes or the same kind

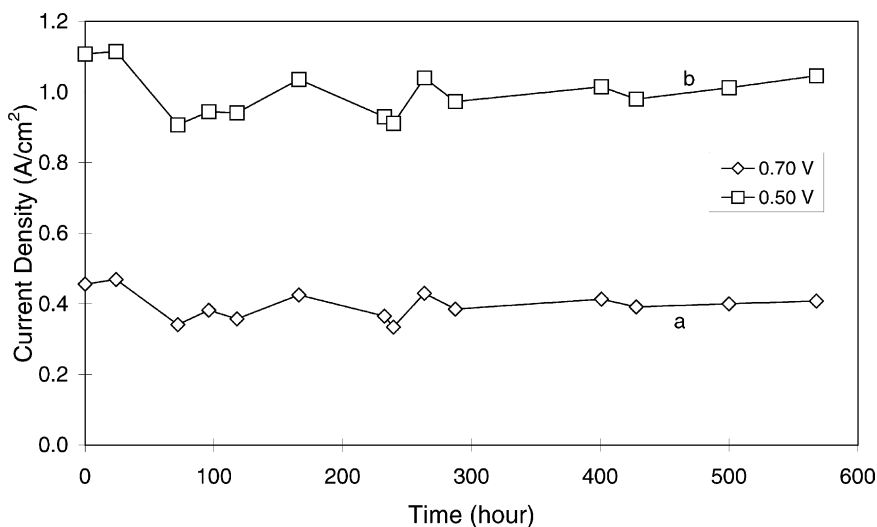


Fig. 3. Current densities of an activated cell at (a) 0.7 and (b) 0.5 V, respectively, within 4 weeks during which period the cell was shut down/restarted numerous times. Nafion 112 membrane, Pt = 0.12 mg/cm².

of membranes but with different thickness and equivalent weight are all able to be activated quickly.

It is proposed that the activation process increases catalyst utilization by opening many “dead” regions in the catalyst layer. Although a proton conductor such as Nafion is mixed into a catalyst layer to make it conduct proton in three dimensions, many of the catalyst sites are not available for reaction due to various reasons. The reasons could be (1) reactants can not reach the catalyst sites because they are blocked, (2) Nafion near these catalyst sites can not be easily hydrated, or (3) an ionic or electronic continuity is not established to these sites. When a fuel cell is operated at elevated temperature and pressurized, many of these “dead” regions are “opened” and then become active.

3. Conclusions

The performance of a low temperature PEM fuel cell can be enormously improved by first operating the cell at an elevated temperature and pressure. Such a procedure is applicable to all kinds of membrane-electrode assemblies

whose electrodes are made using either supported or unsupported catalysts, and the effect achieved is permanent.

References

- [1] A.K. Shukla, P. Stevens, A. Hamnett, J.B. Goodenough, *J. Appl. Electrochem.* 19 (1989) 383.
- [2] E.A. Ticianelli, C.R. Derouin, A. Redondo, S. Srinivasan, *J. Electrochem. Soc.* 135 (1988) 2209.
- [3] Z. Poltarzewski, P. Staiti, V. Alderucci, W. Wieczorek, N. Giordano, *J. Electrochem. Soc.* 139 (1992) 761.
- [4] M.S. Wilson, S. Gottesfeld, *J. Electrochem. Soc.* 139 (1992) L28.
- [5] M.S. Wilson, S. Gottesfeld, *J. Appl. Electrochem.* 22 (1992) 1.
- [6] M. Uchida, Y. Aoyama, N. Eda, A. Ohta, *J. Electrochem. Soc.* 142 (1995) 463.
- [7] J. Fournier, G. Faubert, J.Y. Tilquin, R. Cote, D. Guay, J.P. Dodelet, *J. Electrochem. Soc.* 144 (1997) 145.
- [8] S.J. Lee, S. Mukerjee, J. McBreen, Y.W. Rho, Y.T. Kho, T.H. Lee, *Electrochim. Acta* 43 (1998) 3693.
- [9] E. Passalacqua, F. Lufrano, G. Squadrito, A. Patti, L. Giorgi, *Electrochim. Acta* 43 (1998) 3665.
- [10] Y.-G. Chun, C.-S. Kim, D.-H. Peck, D.-R. Shin, *J. Power Sources* 71 (1998) 174.
- [11] X. Cheng, B. Yi, M. Han, J. Zhang, Y. Qiao, J. Yu, *J. Power Sources* 79 (1998) 75.