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Journal of Power Sources 114 (2003) 21–31

JOURNAL OF POWER SOURCES

www.elsevier.com/locate/jpowsour

Quick and effective activation of proton-exchange membrane fuel cells

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Received 17 September 2002; accepted 30 September 2002

Abstract

It was found that operating a proton-exchange membrane fuel cell at elevated temperature and pressure could largely activate it. When the fuel cell was tested again at ambient conditions, its performance was much higher than that before the activation procedure was performed. Without the activation, the fuel cell could probably never achieve the enhanced performance if only a traditional break-in procedure was performed. The activation procedure normally did not need to exceed 2 h, and it was applicable to all the catalysts, electrodes, catalyst-coated membranes (CCMs), and membrane-electrode assemblies studied.

Keywords: Proton-exchange membrane fuel cell; Activation; Catalyst-coated membrane; Membrane-electrode assembly

1. Introduction

A proton-exchange membrane (PEM) fuel cell is the most promising type of fuel cells that can be used at low temperatures (e.g. from 0 °C and up). The low operating temperature enables it to start up quickly, and thus a PEM fuel cell is a very suitable power source for potable electronics, transportation, and small residences.

The electrical and thermal energy is generated by a component called membrane-electrode assembly (MEA). An MEA is composed of an anode for the fuel oxidation, a cathode for oxygen reduction, and an ion-conducting membrane for proton transportation. The membrane also prevents an electrical short-circuiting between the anode and the cathode, and separates the fuel from the oxidant.

Since the fuel oxidation reaction (1) and the oxygen reduction reaction (2):

$$\text{anode}: \quad H_2 \rightarrow 2H^+ + 2e^- \tag{1}$$

$$\text{cathode}: \quad \tfrac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \tag{2}$$

are kinetically slow, catalysts, such as platinum and its alloys are used to catalyze these reactions. In a fuel cell, the catalysts are made into porous layers to increase the contact area between the reactants and the catalyst particles. The layers can be made onto either the membrane or a gas diffusion medium. Carbon paper and carbon cloth-type materials are the prevalent gas diffusion media thanks to their good electrical and thermal conductivities, high corrosion resistance, and controllable porosity.

In order to reduce the cost of a fuel cell, one approach is to reduce the amount of noble metal catalysts used in the catalyst layers. Metal black with lower surface area was initially used to make the catalyst layer. The catalyst loading in such an electrode needed to be over 4.0 mg/cm^2 in order to achieve good performance. Later on, much smaller metal nanoparticles with higher surface area were prepared onto a support [1–3]. The support has several functions. It provides sites for anchoring the metal particles during and after their formation. The particles formed in such an environment have a small and uniform size. Second, due to the chemical/physical interaction between the support and the metal particles, particle coalescence or aggregation becomes less likely; and therefore, the catalyst does not lose its surface area as fast as the unsupported catalyst. Third, the support provides electrical connection for catalyst particles supported on different support particles. Carbon black is the most practical support used in PEM fuel cells because of its large surface area, good electrical and thermal conductivities, and high corrosion resistance.

Since both electrons and protons are involved in fuel cell reactions as shown by Eqs. (1) and (2), electrical as well as proton conductivity is needed within the catalyst layers. 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

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0378-7753/03/$ – see front matter
PII: S0378-7753(02)00587-6

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 high current density. The catalyst that was not in contact with the membrane was simply wasted.

The situation has been changed when an ionic conductor, such as Nafion®, a perfluorinated ionomer, made by E.I. DuPont, is incorporated into the catalyst layers [4–18]. After Nafion® incorporation, the entire catalyst layer conducts both electrons and protons; hence, the catalyst utilization in the layer is improved dramatically. The catalyst layer can in turn generate and sustain a higher current density.

Nafion® can be impregnated into a catalyst layer by brushing or spraying Nafion® solution onto it, or by floating/dipping the electrode upon/within a Nafion® solution [4–8]. The advantage of this method is that a water-repelling agent, such as polytetrafluoroethylene (PTFE) can be incorporated into the catalyst layer before the application of Nafion®; so that the final catalyst layer will have a controllable hydrophobicity to reduce the likelihood of flooding. The disadvantage of this method is that it is very difficult to control the amount of Nafion® applied, and that it is impossible to have a homogeneous distribution of Nafion® within the entire catalyst layer. The regions with more Nafion® may be too easy to be flooded, while the regions with insufficient Nafion® may not be able to provide enough proton conductivity. Nafion® may localize on surface of the catalyst layer in one place but penetrate the underlying gas diffusion medium in another place.

Another method to incorporate Nafion® into catalyst layers is to mix catalysts, especially supported catalysts, with Nafion® directly; and then the resulting mixture is used to make the catalyst layer [8–18]. Since the catalyst and Nafion® can form a pretty good mixture, Nafion® and catalyst achieve a more even distribution throughout the entire catalyst layer. Solvents, such as glycerol may be used during the mixing in order to achieve a good viscosity and to hold the catalyst particles in suspension to minimize their agglomeration [8–12]. Sometimes, Nafion® solution is converted into a colloid first by adding a proper organic solvent before mixing it with the catalyst [13,15]. It was claimed that colloidal Nafion® could form a good network to achieve a uniformity of distribution on the catalyst particles. High performance electrodes can also be prepared without adding any additional organic solvents [18].

When a Nafion® solution or colloid is directly mixed with the catalyst, it is difficult to incorporate PTFE into the catalyst layer because a following step of sintering PTFE at a temperature higher than 330 °C will destroy Nafion®. Without PTFE, the catalyst layer is more likely to be flooded, so it needs to be made thin.

When a PEM fuel cell is tested, it does not reach the best performance immediately. A so-called pre-conditioning or break-in period is needed. During this period, the cell performance normally increases gradually. Depending on the MEAs, a pre-conditioning could take several days or even longer to complete. This not only consumes a lot of hydrogen fuel, but also slows down the entire production process.

When operated under ambient temperature and pressure, the performance of an MEA consisting of low catalyst loading electrodes made from carbon-supported catalysts was much lower than that of an MEA consisting of high catalyst loading electrodes made from Pt black. Although a standard brink-in process could increase the fuel cell performance, the increase was very limited.

Recently, we discovered several methods that could increase the performance of a PEM fuel cell, especially those with low catalyst loadings [19–21]. One of the methods is treating electrodes or MEAs using hot water or steam before they are assembled into a stack or a test fixture [19]. Another method is generating hydrogen (e.g. hydrogen evolution) within the electrode that is intended to be activated via the reduction of protons using an external power source [20]. A third method is operating the MEA at elevated temperature and pressure before it is operated at ambient conditions [21].

The third activation procedure was briefly discussed in a short communication [21]. This was the most effective one among these three methods, and the activation result was permanent [21]. The current paper reports this method in details. The results on a variety of catalysts, electrodes, catalyst-coated membranes (CCMs), and MEAs will be presented.

2. Experimental

Catalyst mixtures were prepared by directly mixing supported catalysts with Nafion® solution [18]. The Nafion® content within the mixture was controlled at 30%. The mixture was stirred thoroughly before it was applied onto a gas diffusion medium, such as ELAT or carbon paper. The electrodes were dried in an oven at 135 °C for 30 min, and then were hot-bonded onto a Nafion® membrane at 130 °C for 3 min.

Single cell tests were performed using a homemade 10 cm^2 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 reactants. They were humidified by passing through stainless steel water bottles prior to entering the cell. The cell temperature, hydrogen humidification temperature, air humidification temperature, hydrogen back pressure, and air back pressure are denoted hereinafter as $T_{cell}/T_{hydrogen}/T_{air}$, $P_{hydrogen}/P_{air}$. For example, a cell temperature of 75 °C, hydrogen humidification temperature of 95 °C, air humidification temperature of 90 °C, hydrogen back pressure of 20 psig, and air back pressure of 30 psig, are expressed as 75/95/90 °C, 20/30 psig. The stoichiometries of air and hydrogen were controlled using flow meters

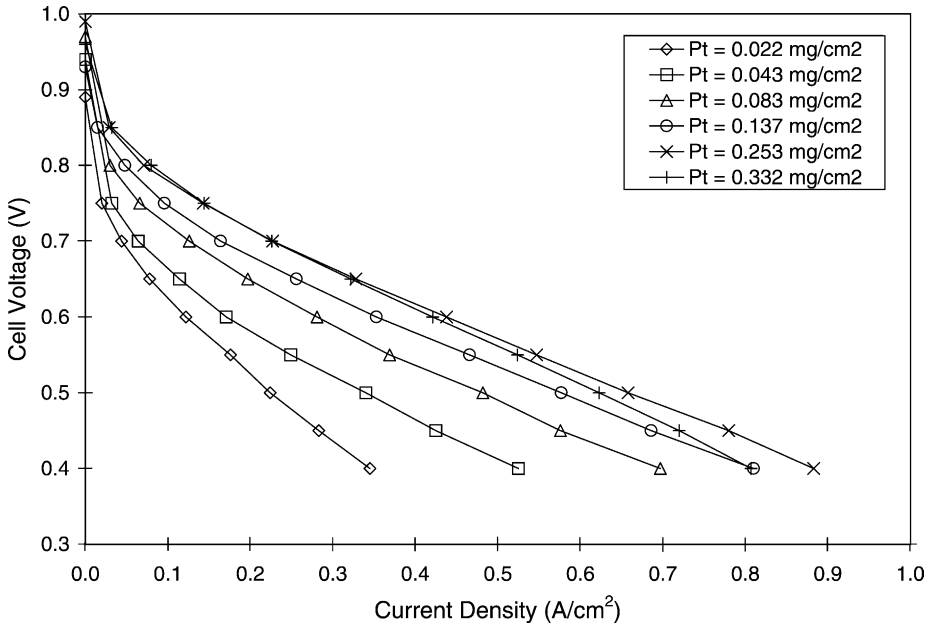

Fig. 1. Performance of electrodes with various Pt loadings made using E-TEK 20% Pt/C before activation. 35/45/45 °C; Nafion® 112 membrane; ELAT gas diffusion medium.

to about 10 at a current density of 2.0 A/cm^2. The load was varied using a rheostat when voltage (V)–current density (I) curves were collected.

When pure hydrogen is used as the fuel, the entire fuel cell performance is determined by the cathode. Therefore, the following studies only specify the catalyst loading of the cathode.

3. Results and discussion

Fig. 1 shows the performance of a variety of cathodes with Pt loadings ranging from 0.022 to 0.332 mg/cm^2, made using E-TEK 20% Pt/Vulcan XC-72. The results were taken after the cells had been tested at 35/45/45 °C for several hours until no further increase in performance

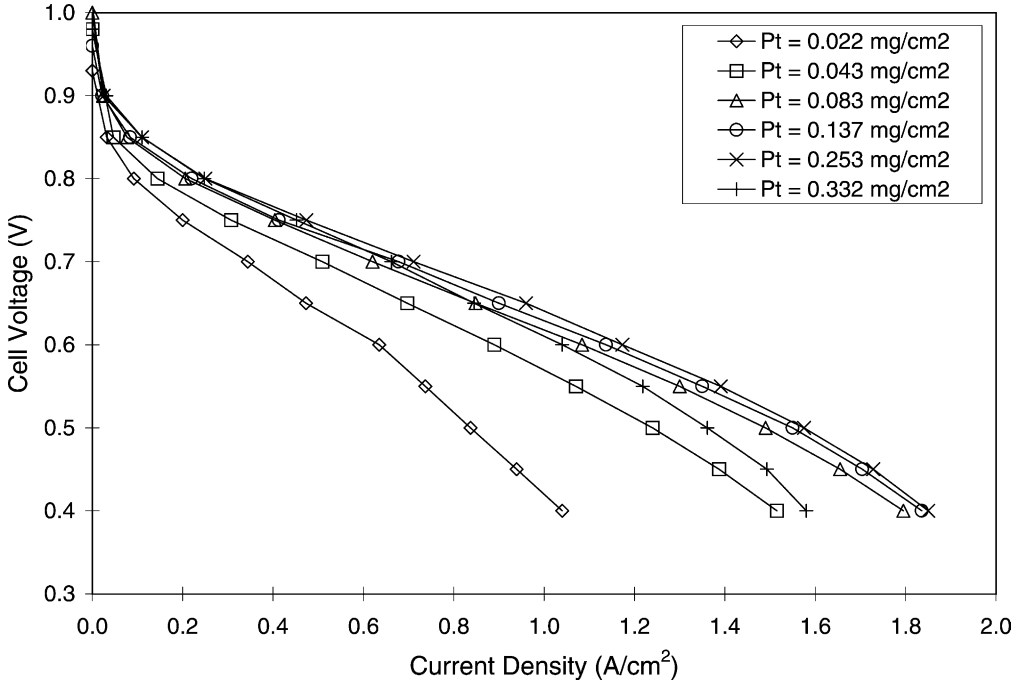

Fig. 2. Performance of electrodes with various Pt loadings made using E-TEK 20% Pt/C during activation. 75/95/90 °C; Nafion® 112 membrane; ELAT gas diffusion medium.

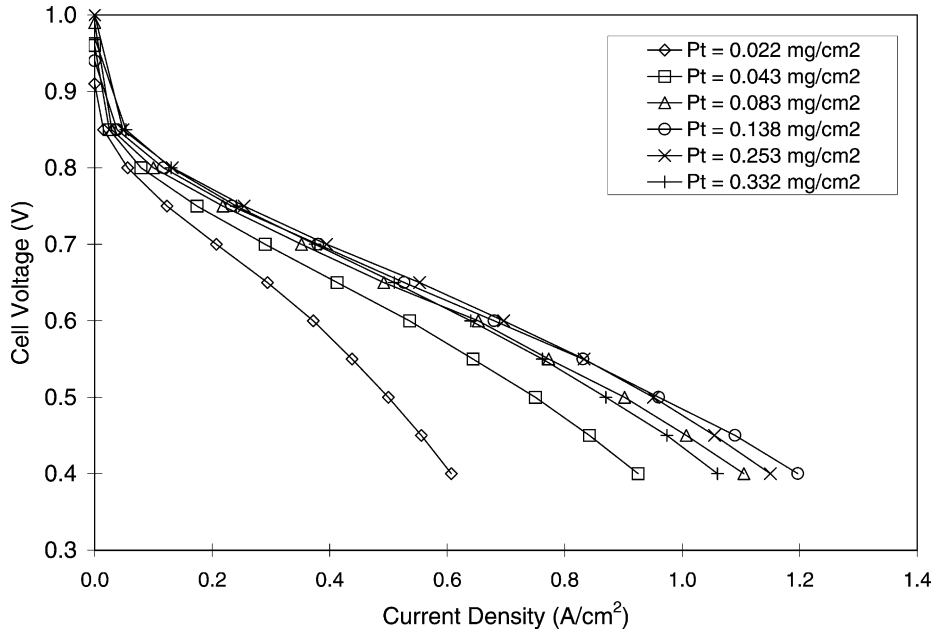

Fig. 3. Performance of electrodes with various Pt loadings made using E-TEK 20% Pt/C after activation. 35/45/45 °C; Nafion® 112 membrane; ELAT gas diffusion medium.

was observed. In other words, this was the best performance that could be achieved after a standard break-in process. The fuel cell performance increased pretty evenly with the Pt loading up to 0.253 mg/cm^2, and a further increase to 0.332 mg/cm^2 caused a slight decline in performance. This decline could be due to increase in catalyst layer's electric and ionic resistance, and to the increase in mass transport limitation.

These MEAs were then activated at 75/95/90 °C, 20/30 psig for about 2 h. The performance under such a condition is presented in Fig. 2. Since both temperature and pressure favor the electrochemical reactions, it is not surprising to see much higher performance than in Fig. 1. Under this condition, the performance increased largely from a Pt loading of 0.022–0.083 mg/cm^2, but further increasing Pt loading to 0.253 mg/cm^2 only resulted in slight better

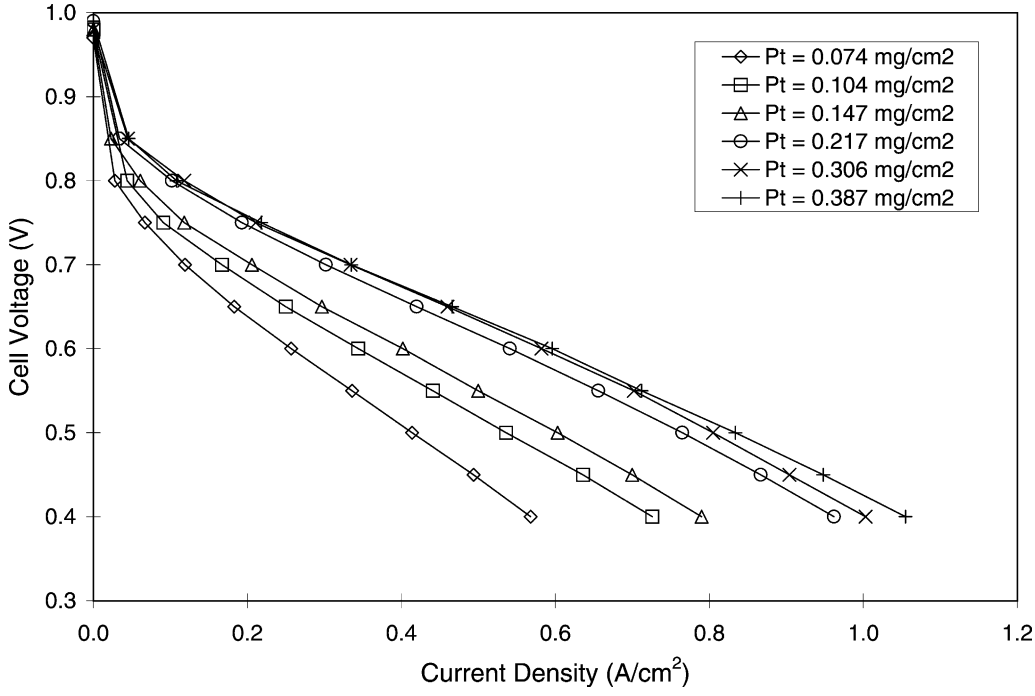

Fig. 4. Performance of electrodes with various Pt loadings made using E-TEK 40% Pt/C before activation. 35/45/45 °C; Nafion® 112 membrane; ELAT gas diffusion medium.

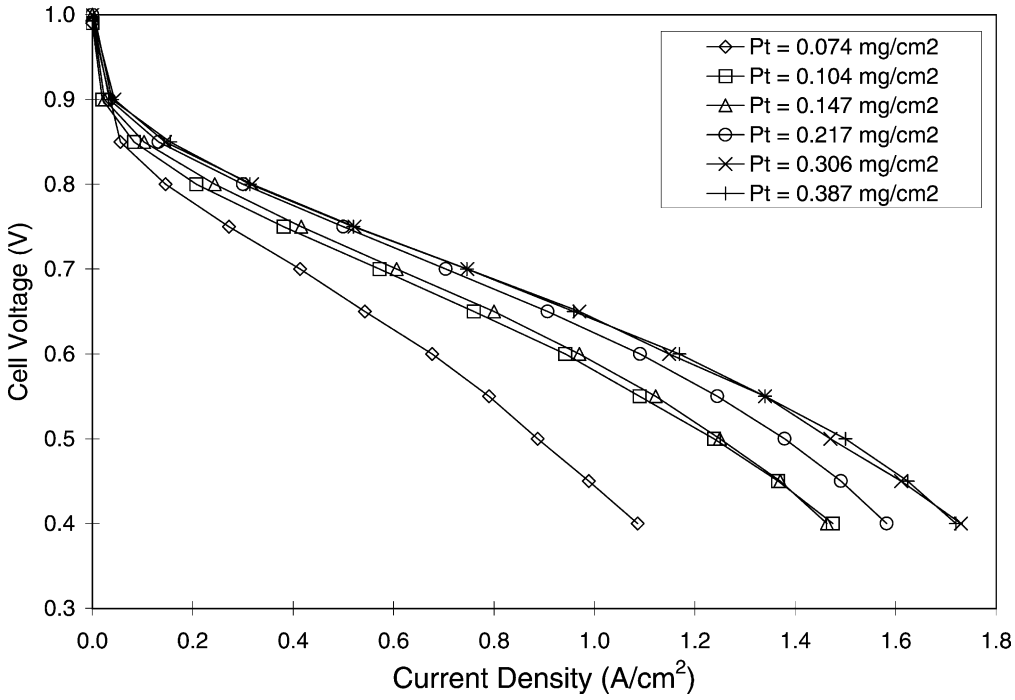

Fig. 5. Performance of electrodes with various Pt loadings made using E-TEK 40% Pt/C during activation. 75/95/90 °C; Nafion® 112 membrane; ELAT gas diffusion medium.

performance. When Pt loading was increased to 0.332 mg/cm^2, the performance declined.

After the activation step, the testing condition was returned to 35/45/45 °C from 75/95/90 °C, 20/30 psig, and Fig. 3 shows the performance. Surprisingly, the performance was much higher than that before activation (Fig. 1), even though the tests were carried out under the same conditions. Such an enhanced performance could probably never be

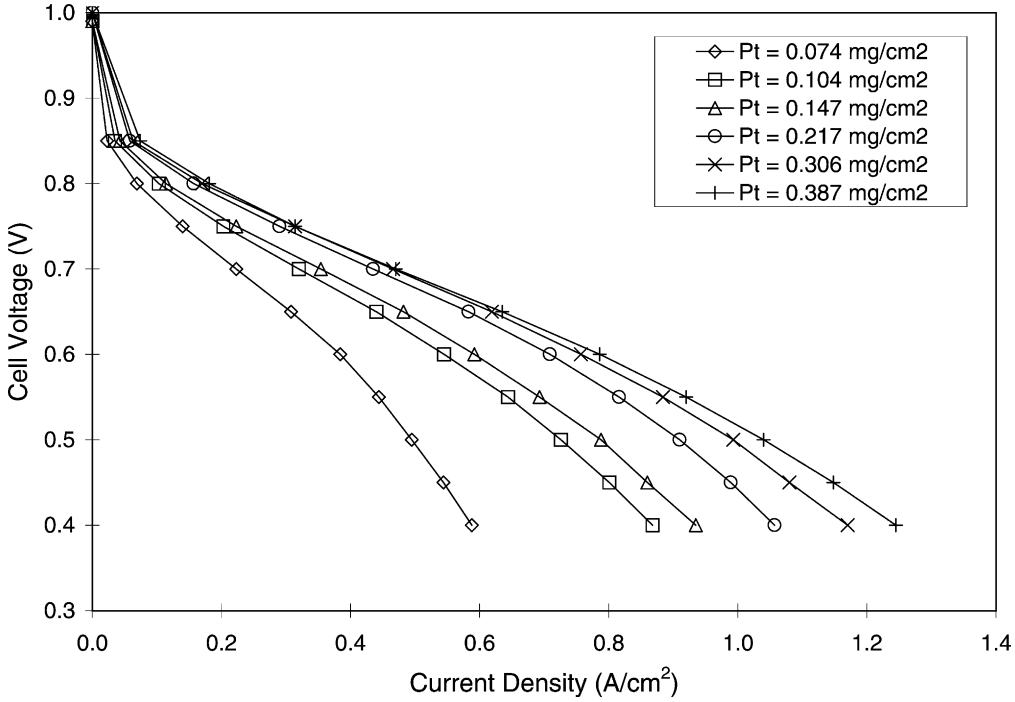

Fig. 6. Performance of electrodes with various Pt loadings made using E-TEK 40% Pt/C after activation. 35/45/45 °C; Nafion® 112 membrane; ELAT gas diffusion medium.

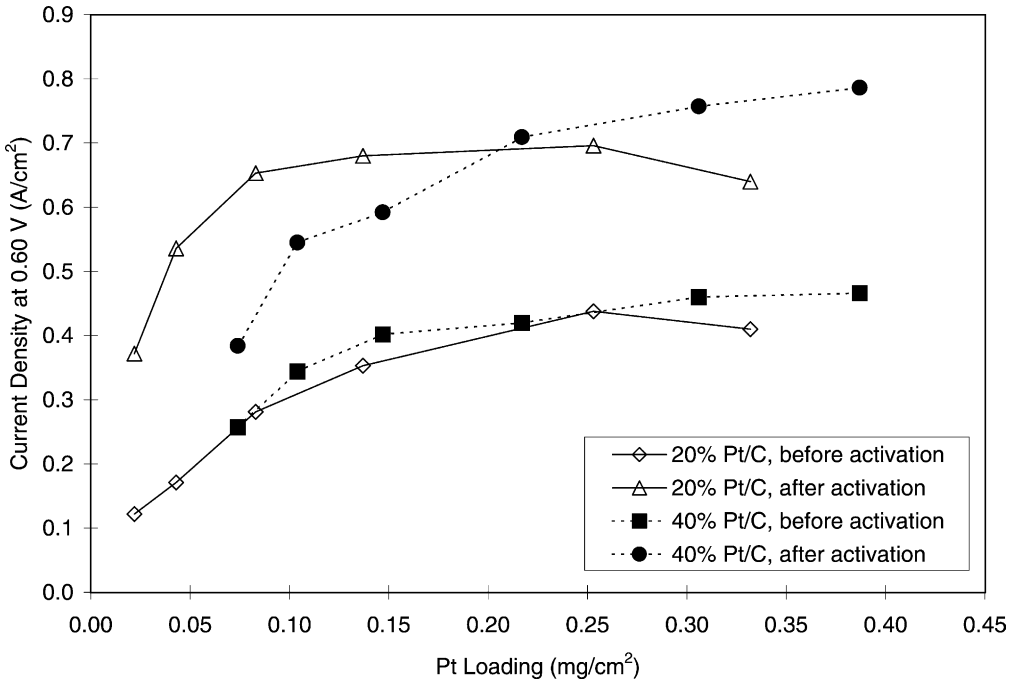

Fig. 7. Current density at 0.60 V vs. Pt loading for electrodes made using either 20 or 40% E-TEK Pt/C. 35/45/45 °C; Nafion® 112 membrane; ELAT gas diffusion medium.

achieved by a normal break-in procedure, no matter how long that procedure would be performed. Clearly, exposing MEAs at elevated temperature and pressure results in their activation. This activation is largely different from a traditional break-in procedure.

Fig. 3 also shows that after activation the increase in performance with Pt loading behaved largely different from that before activation, but was quite similar to that during the activation step. When Pt loading was increased from 0.022 to 0.083 mg/cm^2, large performance increase was observed. Further increasing Pt loading to 0.253 mg/cm^2 only resulted in slight increase; and even further increasing Pt loading to 0.332 mg/cm^2 caused the performance to decline. Apparently, the activation process changed the electrode, and such a change was maintained when the activation procedure was removed.

Electrodes with Pt loadings ranging from 0.074 to 0.387 mg/cm^2 made using 40% E-TEK Pt/Vulcan XC-72 were also tested. Figs. 4–6 show the performance before, during, and after activation. There was no doubt again that the fuel cell performance increased dramatically after activation.

Fig. 7 plots the fuel cell current density at 0.60 V versus Pt loading before and after activation for both 20 and 40% Pt/Vulcan XC-72. Before activation, both type catalysts seemed to follow a similar trend line. But after the activation, a larger difference was seen. For the 20% Pt/C, after the Pt loading reached 0.083 mg/cm^2, the performance approached the plateau. For the 40% Pt/C, the Pt loading needed to be higher than 0.217 mg/cm^2 to approach the plateau. Hence, using 20% Pt/C could save at least 50% Pt without sacrificing the fuel cell performance. Table 1 summarizes the results shown in Fig. 7.

It was found that the activation procedure normally did not need to be over 2 h when performed at 75/95/90 °C, 20/30 psig. Fig. 8 shows the performance of an MEA (cathode Pt loading = 0.17 mg/cm^2, E-TEK 20% Pt/Vulcan XC-72) before, during, and after activation. It can be seen that a 30 min activation nearly fully activates the MEA. Of course, at lower temperature and pressure, a slightly longer activation time will be needed.

In order to test the versatility of this activation method, a variety of catalysts, electrodes, CCMs, and MEAs were evaluated.

Table 1
Performance before and after activation for E-TEK 20 and 40% Pt/Vulcan XC-72

20% Pt/C			40% Pt/C		
Pt (mg/cm^2)	Current density at 0.60 V (A/cm^2)		Pt (mg/cm^2)	Current density at 0.60 V (A/cm^2)	
	Before activation	After activation		Before activation	After activation
0.022	0.122	0.372	0.074	0.257	0.384
0.043	0.171	0.536	0.104	0.344	0.545
0.083	0.281	0.653	0.147	0.297	0.592
0.137	0.353	0.680	0.217	0.420	0.709
0.253	0.438	0.696	0.306	0.460	0.757
0.332	0.410	0.640	0.387	0.466	0.786

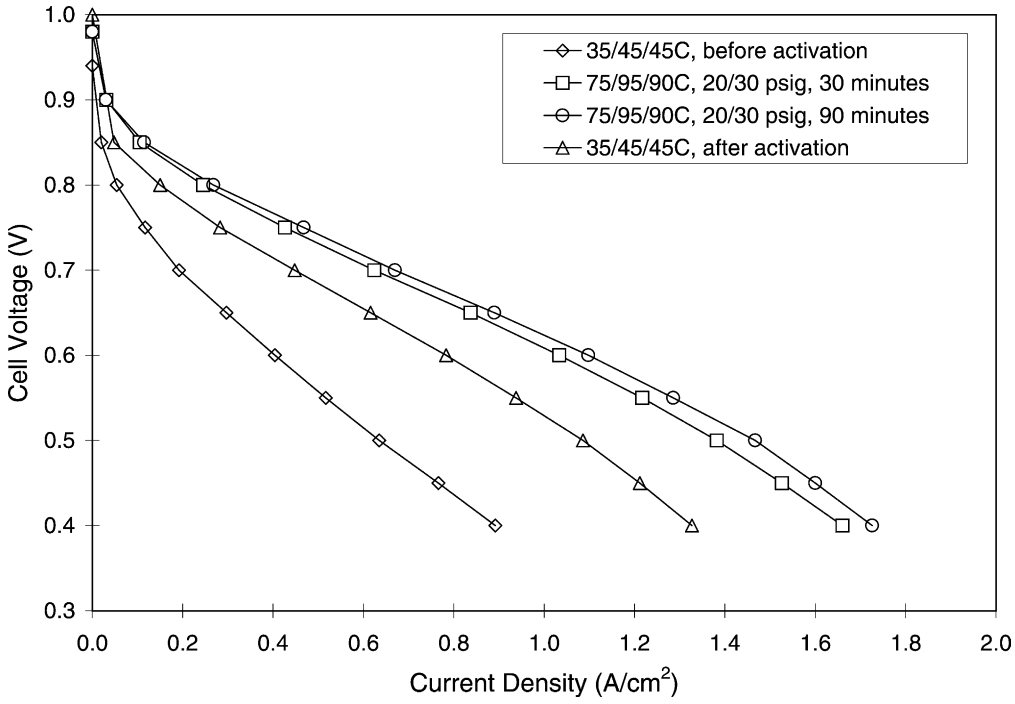

Fig. 8. Effect of activation time on performance. E-TEK 40% Pt/C; Pt loading 0.17 mg/cm^2; Nafion® 112 membrane; ELAT gas diffusion medium.

Figs. 9–11 illustrate the performance of electrodes fabricated following a Los Alamos method by adding glycerol into catalyst mixtures [9,10]. However, instead of applying the catalyst mixture onto a decal then transferring it onto a membrane, the catalyst mixture was directly applied onto the gas diffusion medium, ELAT. The catalyst used was E-TEK 20% Pt/Vulcan XC-72. Evidently, the performance of all the four electrodes increased largely after activation, and the electrode with a Pt loading of 0.122 mg/cm^2 gave the best performance. It is expected that the structure of such a

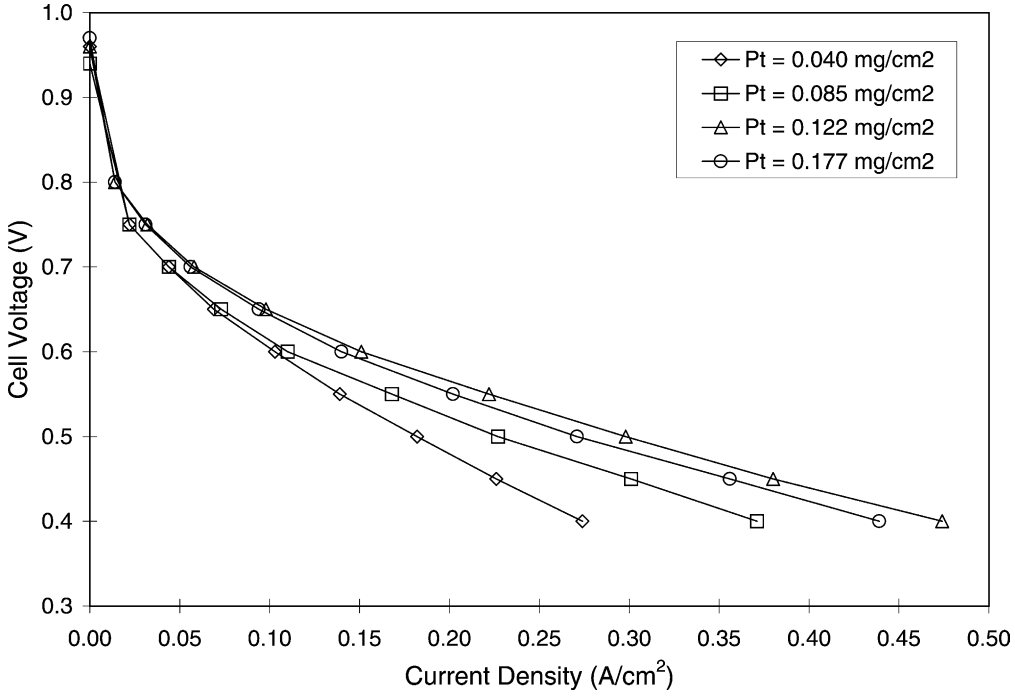

Fig. 9. Performance of electrodes fabricated by following a LANL's method where glycerol was added when catalyst mixtures were prepared—before activation. E-TEK 20% Pt/C; 35/45/45 °C; Nafion® 112 membrane; ELAT gas diffusion medium.

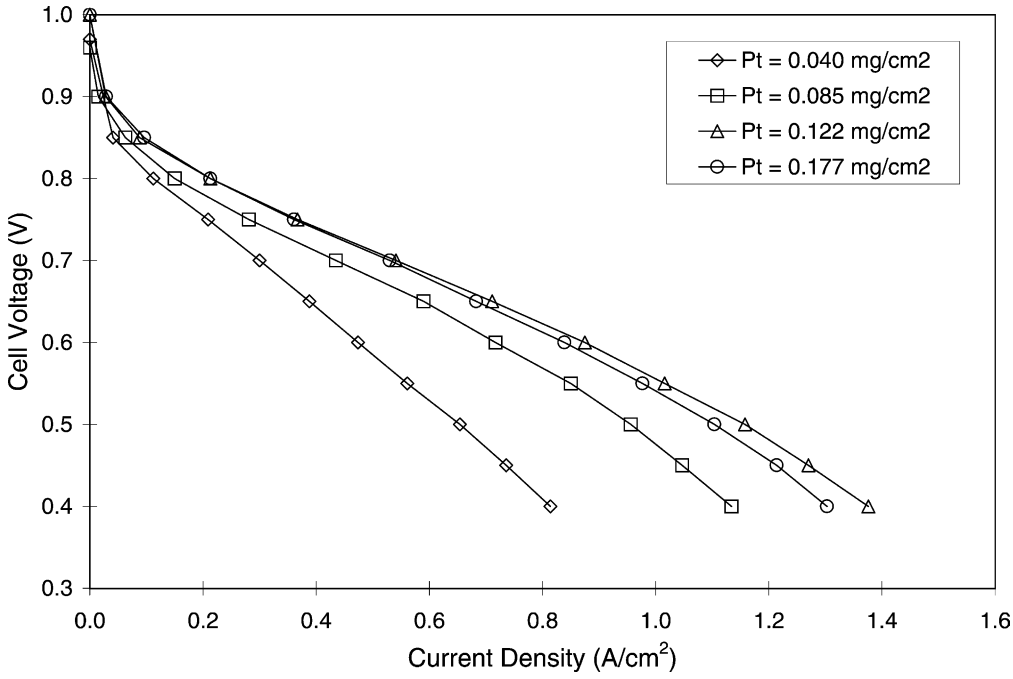

Fig. 10. Performance of electrodes fabricated by following a LANL's method where glycerol was added when catalyst mixtures were prepared—during activation. E-TEK 20% Pt/C; 75/95/90 °C; Nafion® 112 membrane; ELAT gas diffusion medium.

catalyst layer will possess some difference from that without adding glycerol. Nevertheless, they could all be effectively activated.

Electrodes and CCMs obtained from other fuel cell developers were also tested. For those electrodes or CCMs, besides the Pt loadings, we did not know the type of catalysts, the components and their amounts within the catalyst layers, and the procedure used to make them.

The effect of activation on performance of one such electrode is shown in Fig. 12, where the cathode had a Pt

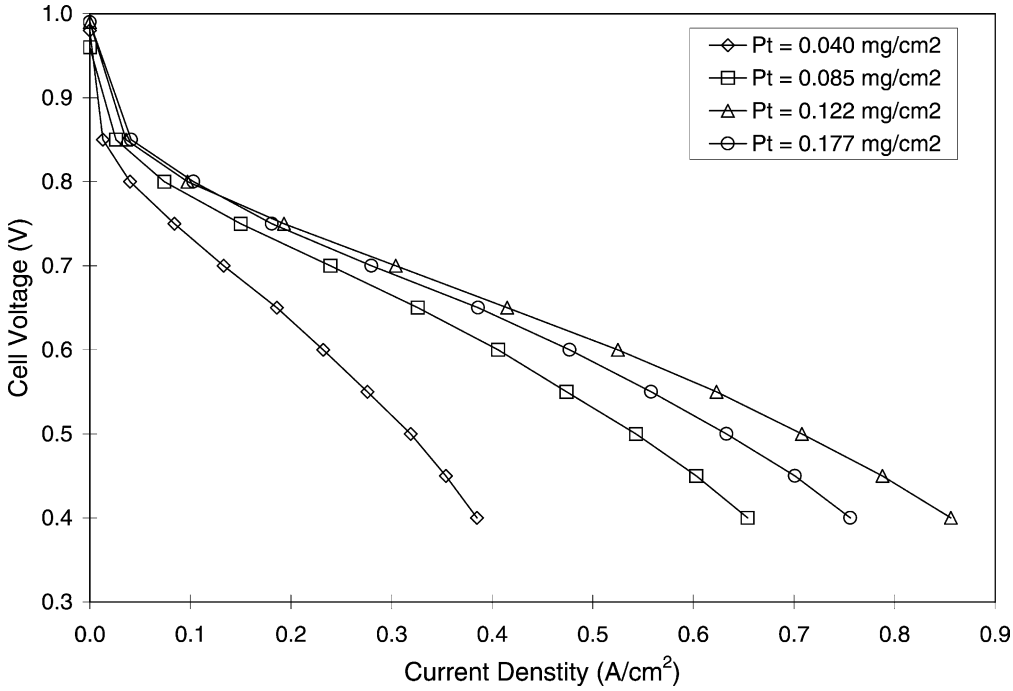

Fig. 11. Performance of electrodes fabricated by following a LANL's method where glycerol was added when catalyst mixtures were prepared—after activation. E-TEK 20% Pt/C; 35/45/45 °C; Nafion® 112 membrane; ELAT gas diffusion medium.

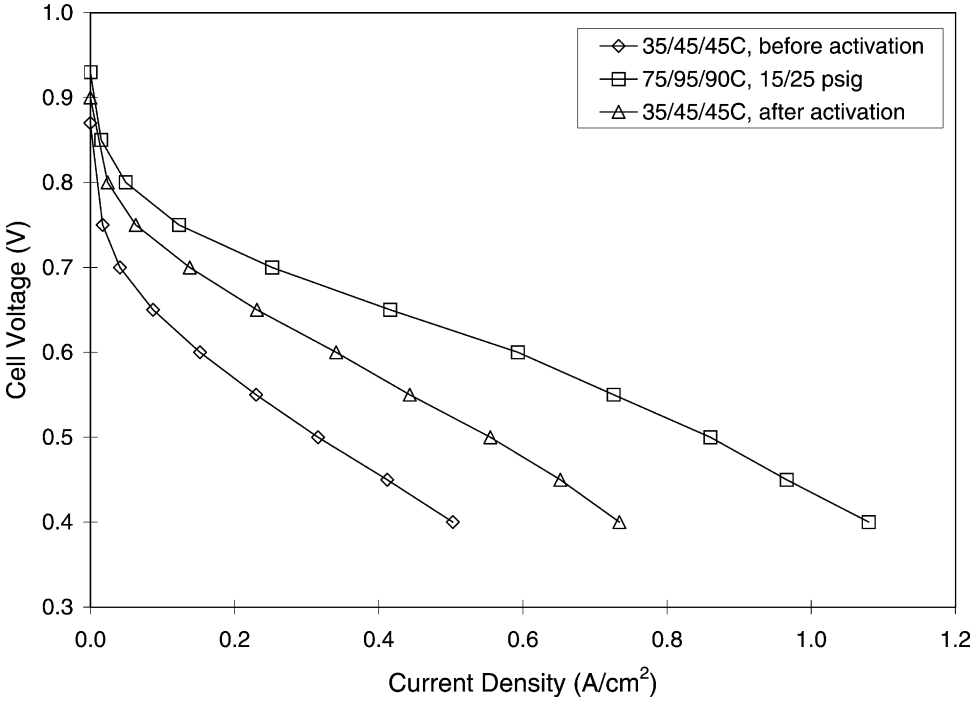

Fig. 12. Effect of activation on performance of an electrode obtained from another fuel cell developer. Pt loading 0.40 mg/cm^2; Nafion® 112 membrane; carbon paper gas diffusion medium.

loading of 0.40 mg/cm^2. The effect of activation on performance of a CCM with a Pt loading of 0.35 mg/cm^2 is shown in Fig. 13. Clearly, in both cases, large increase in performance was obtained after the activation step. When the above CCM was tested, two pieces of gas diffusion medium was attached to the CCM without any bonding between them.

The activation procedure also works on electrodes made using Pt black, as shown in Fig. 14, where the cathode had a Pt loading of 1.7 mg/cm^2. The performance increase caused

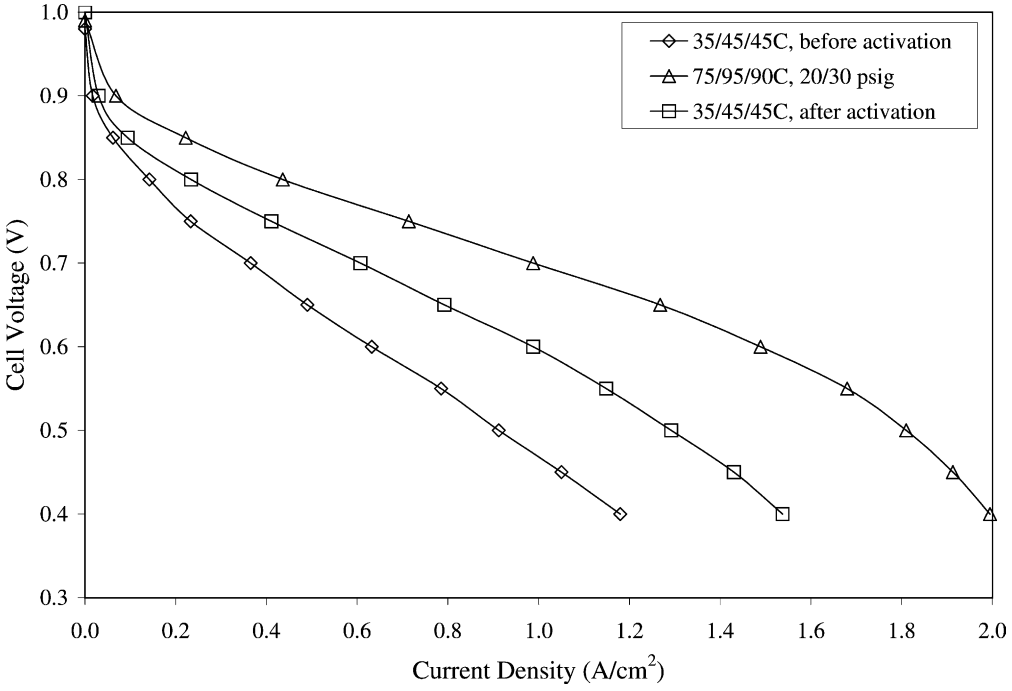

Fig. 13. Effect of activation on performance of a catalyst-coated membrane obtained from another fuel cell developer. Pt loading 0.35 mg/cm^2; Nafion® 112 membrane; Toray paper gas diffusion medium.

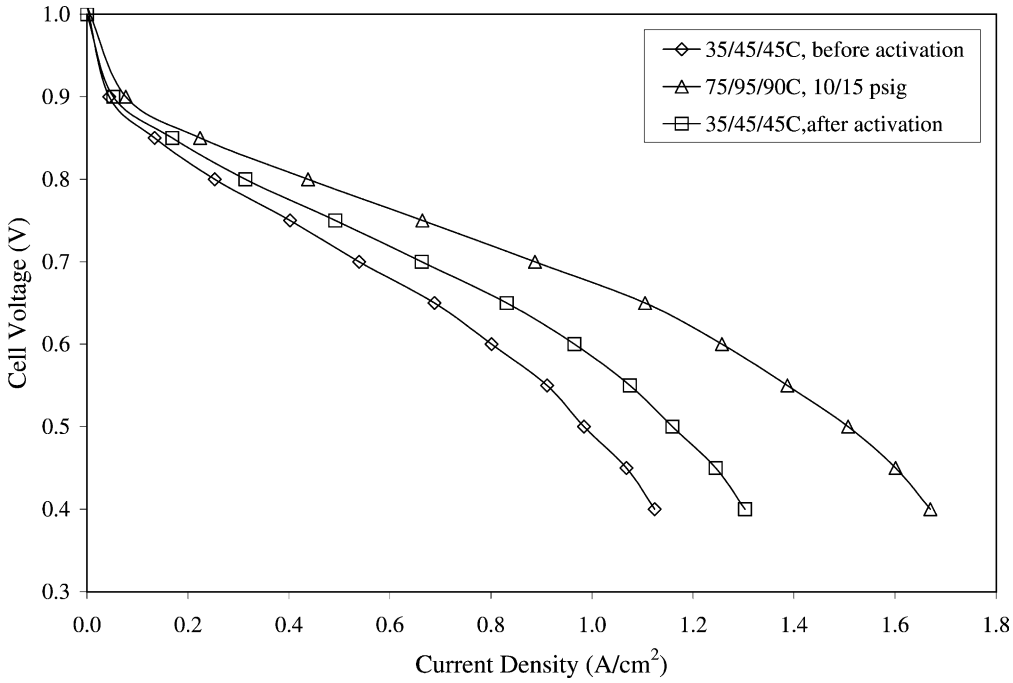

Fig. 14. Effect of activation on performance of an electrode made using Pt black. Pt loading 1.7 mg/cm^2; Nafion® 112 membrane; Toray paper gas diffusion medium.

by activation was normally smaller for this kind of electrode than for electrodes made using carbon-supported catalysts.

The activation procedure is also effective to electrodes made on different gas diffusion medium, as shown in Fig. 15, where carbon paper from either Toray or Spectracorp was used.

The activation procedure also operates efficiently on MEAs consisting of different membranes, as shown in Fig. 16, where Nafion® 111 and 112 were used as membranes. The higher performance of Nafion® 111 membrane was because of its lower ionic resistance.

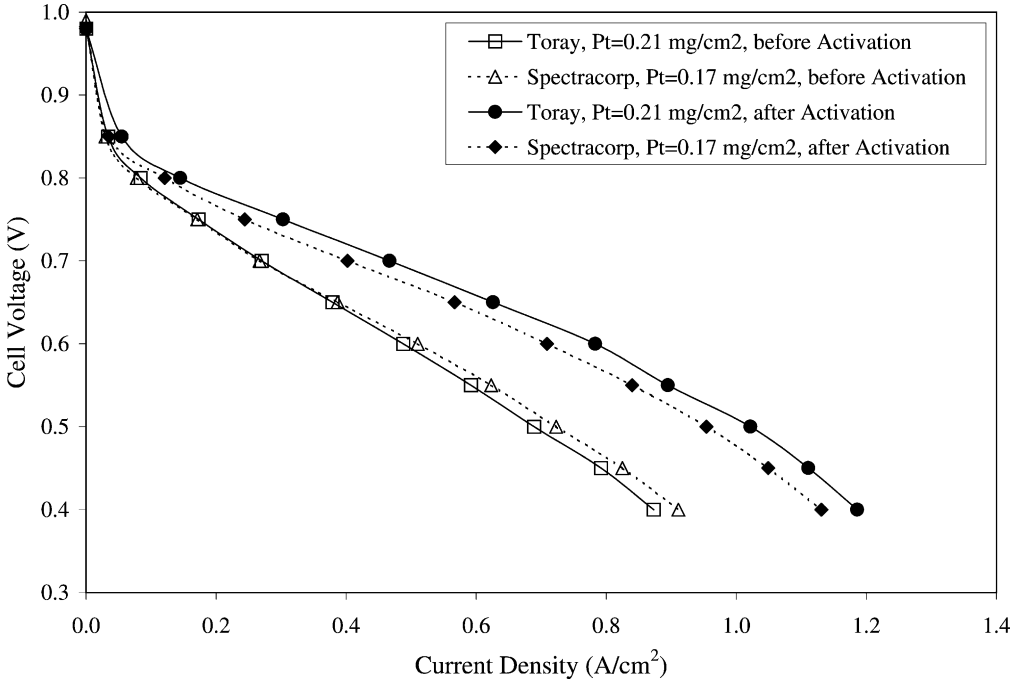

Fig. 15. Effect of activation on performance of electrodes prepared on different gas diffusion media. 35/45/45 °C; Johnson Matthey 20% Pt/C; Nafion® 112 membrane; activation was performed at 75/95/50 °C and 15/20 psig.

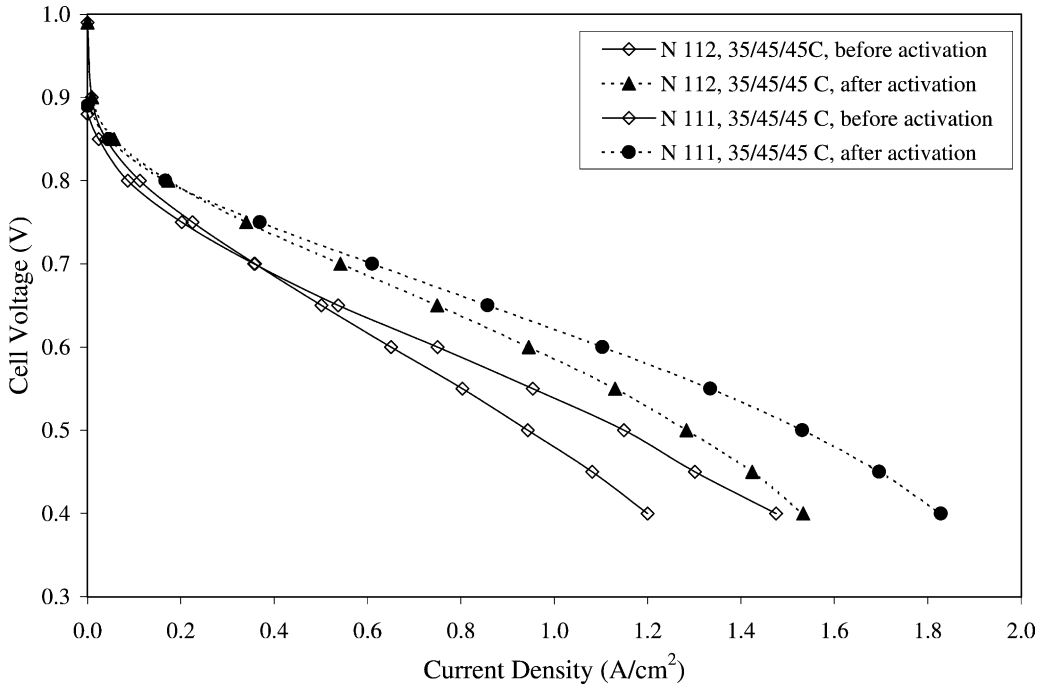

Fig. 16. Effect of activation on performance of MEAs with Nafion® 111 and 112 as the membrane, respectively. 35/45/45 °C; Engelhard 40% Pt/C; ELAT gas diffusion medium; activation was performed at 75/95/50 °C and 20/30 psig.

4. Conclusions

A variety of electrodes and MEAs were activated by operating the fuel cells at elevated temperature and pressure. The activation procedure was applicable to different catalysts, membranes, gas diffusion media, and catalyst layer structures. The activation process normally did not need to exceed 2 h when performed at 75/95/90 °C and 20/30 psig.

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