Low Pt loading high performance cathodes for PEM fuel cells

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Abstract

A simple direct mixing of carbon-supported catalysts with Nafion without adding any additional organic solvents was used to make electrodes for oxygen reduction in PEM fuel cells. For E-TEK 20% Pt/C, a Nafion content of 30% in the catalyst layer exhibited the best performance. Electrode dried from 90 to 150 °C showed little difference in performance. Highest power densities increased almost linearly with cell temperature, and values of 0.52, 0.60, 0.63, and 0.72 W/cm^2 were achieved at 35, 50, 60, and 75 °C, respectively, for a cathode with a Pt loading of 0.12 mg/cm^2 and operated using air at ambient pressure. A maximum performance was achieved with Pt loadings of 0.20 ± 0.05 and 0.35 ± 0.05 mg/cm^2 for 20 and 40% Pt/C, respectively, while the maximum performance using 40% Pt/C was only slightly better than that using 20% Pt/C. A Nafion/carbon sublayer with up to 30% Nafion content added between ELAT and the catalyst layer did not show any effect on performance.
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1. Introduction

Low Pt loading electrodes can be fabricated by a few novel methods. One method is to impregnate Nafion into a catalyst layer [1]. Nafion can be applied by brushing, spraying, or by floating/dipping the electrode on/in a Nafion solution. The advantage of this method is that PTFE can be incorporated into the catalyst layer before the application of Nafion, so that the final electrode will have a controllable hydrophobicity to reduce the possibility of getting serious flooded. 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 in the entire catalyst layer [2–4]. Another method is to mix supported catalyst with Nafion directly in the presence of glycerol [5,6]. The purpose of adding glycerol is to form a mixture that is relatively viscous and holds the catalyst particles in suspension to minimize their agglomeration [5,6]. A third method also mixes the catalyst with Nafion, but it converts Nafion solution into a colloid by adding a proper organic solvent first before the addition of the

supported catalyst [7]. It was believed that such a procedure resulted in a good network of Nafion to achieve an uniformity of Nafion on the catalyst particles [7]. The disadvantage of the latter two method is that PTFE can not be incorporated into the catalyst layer, so the electrode is prone to flooding. In order to minimize the effect of flooding, the catalyst layer needs to be made thin.

We have prepared electrodes using various methods, including those mentioned above. One of the simplest methods we experimented was to mix supported catalyst with Nafion solution and water without adding any additional organic solvent. This method was not only simpler, safer and more economical, but also achieved better performance. We herein report the details.

2. Experimental

Catalyst mixtures were prepared in the following way: supported catalyst was first added to a cold Nafion solution (5%, DuPont). If the Nafion solution is not cold enough, catalyst burning may occur when the catalyst is added. Another way to prevent catalyst burning is to wet it first with a small amount of water. After a few minutes of stirring, some water was added to dilute the mixture. The mixture

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was then stirred for ca. 30 min, followed by a sonication for at least 1 h. During the sonication, especially in the beginning, the solid materials tended to settle down at the bottom, so a few short, intermittent stirrings were performed throughout the process. After sonication, the mixture became quite viscous, and the solid materials did not separate from the liquid readily. The mixture was kept under stirring prior to application onto ELAT, the gas diffusion medium used as the cathode substrate. The electrode was dried at room temperature for 30 min and then at 135 °C for another 30 min. If the electrode was directly dried at 135 °C, cracks may form in the catalyst layer due to the fast evaporation of solvents, and such cracks will affect the performance of the electrode. Without specification, the carbon-supported catalysts were purchased from E-TEK.

Membrane electrode assemblies (MEAs) were made by hot-bonding electrodes on Nafion membranes at 130 °C for 3 min. The electrode prepared above was used as the cathode, and another electrode with a Pt loading higher than 1.0 mg/cm^2 was used as the anode. The high Pt loading on the anode made it certain that the anode was not limiting the performance of the MEA, as our purpose was to evaluate the cathode. Nafion 112 (DuPont) was used as the membrane for all the MEAs reported here.

MEAs were tested using a home-made 10 cm^2 single cell. The cell was composed of a pair of metal plates with serpentine flow-fields. The plates were coated by a metal nitride for corrosion protection. Air and pure hydrogen were used as the reactants. They were humidified by passing through stainless steel water bottles at temperatures slightly higher than the cell temperature. Most tests were performed using a cell temperature of 35 °C, hydrogen humidification temperature of 45 °C, and air humidification temperature of 45 °C (hereinafter denoted as 35/45/45 °C). The stoichiometries of air and hydrogen were around 10 at a current of 2.0 A/cm^2. The load was varied using a rheostat when voltage (V)–current density (I) curves were collected. The MEAs had been activated by an H Power's proprietary technique before all the data shown below were collected [8].

3. Results and discussion

3.1. Performance versus Nafion content

Incorporation of Nafion into a catalyst layer makes the latter active in three dimensions because proton can then be transported throughout the entire layer. It was reported that the ionic conductivity of such a catalyst layer was proportional to the volume fraction of Nafion in the composite mixture [9]. However, since Nafion is an electronic insulator, it decreases the electronic conductivity of the catalyst layer, and may cause some catalyst particles to be electronically isolated. These isolated particles will not be able to participate in any electrochemical reactions. In addition, Nafion will change the porosity, permeability, and hydrophobicity of the catalyst layer. Therefore, the Nafion content in the catalyst layer needs to be precisely controlled in order to achieve the best balance among all these influencing factors [10–13]. Fig. 1 shows the performance of electrodes with different Nafion contents in the catalyst layers. It can be seen that the performance increased with Nafion content up to 30%, and it decreased afterwards. For the following tests, all the electrodes were made with a Nafion content of 30%.
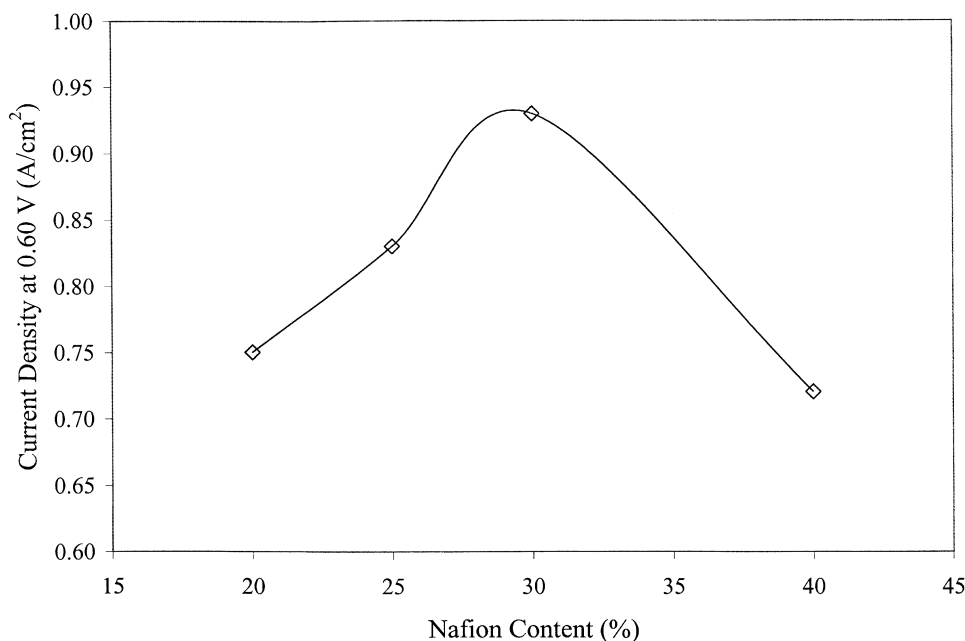

Fig. 1. Effect of Nafion content in the catalyst layer on performance. E-TEK 20% Pt/C, 35/45/45 °C.
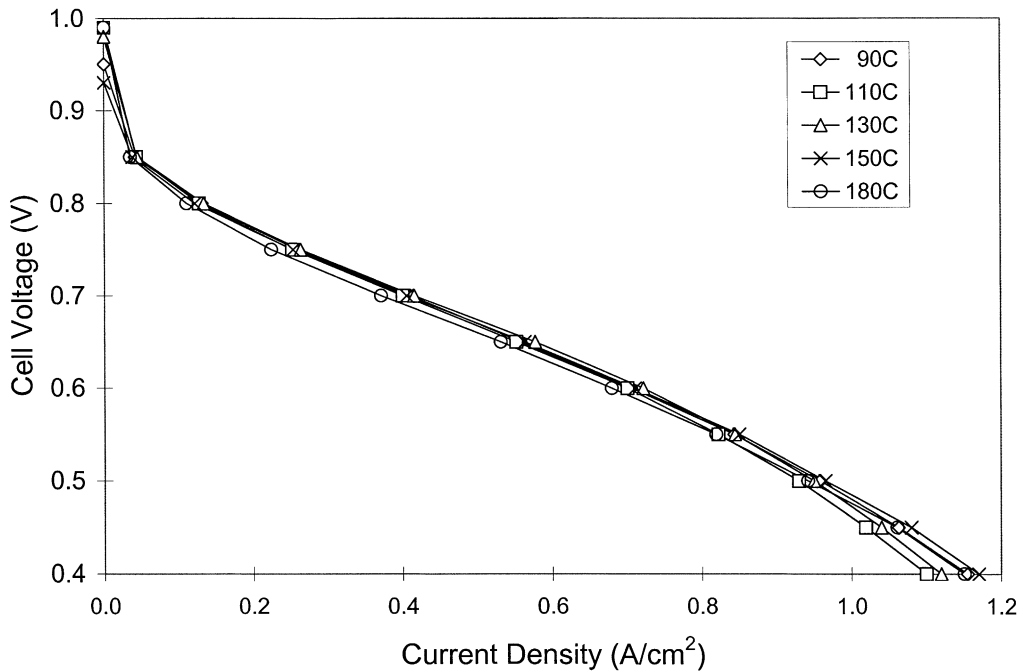
Fig. 2. Effect of electrode drying temperature on performance. E-TEK 20% Pt/C, 35/45/45 °C; Pt = 0.12 mg/cm^2.

3.2. Performance versus electrode drying temperature

After the catalyst layer was applied onto the gas diffusion medium, the electrode was normally left in air for a natural drying before it was dried in an oven. The drying step made Nafion more robust, and then it was less likely to be washed away during the usage. But the drying temperature should not be too high to cause an apparent decomposition of Nafion. Figs. 2 and 3 show the performance of electrodes dried at different temperatures ranging from 90 to 180 °C. Clearly, drying temperature in this range has little effect on

the performance. A closer look indicates that the electrode dried at 180 °C has a slightly lower performance at current densities less than 0.8 A/cm^2. This may be because Nafion dried at such a high temperature is difficult to be fully hydrated. Also, such a drying temperature may cause Nafion to lose some sulfonic acid groups.

3.3. Performance versus cell temperature

The kinetics of oxygen reduction reaction is largely affected by cell temperature, and Fig. 4 shows the performance of
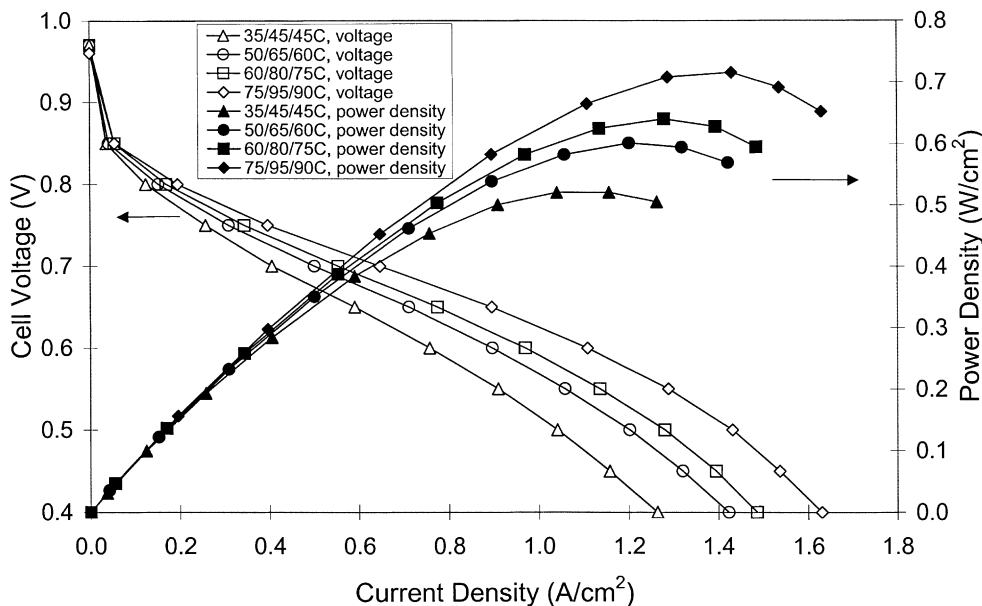

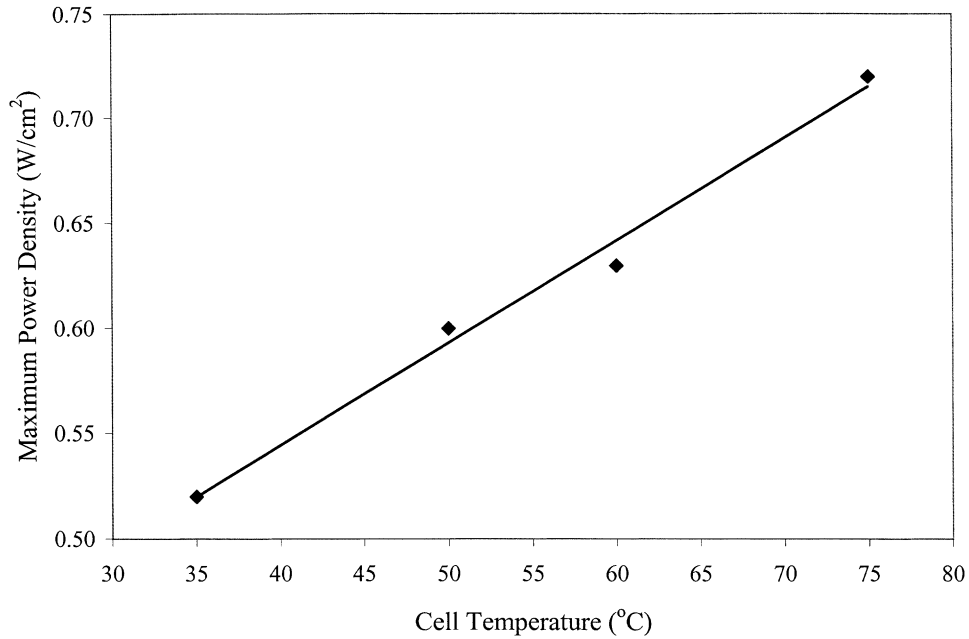Fig. 3. Effect of cell temperature on performance. E-TEK 20% Pt/C; Pt = 0.12 mg/cm^2.

Fig. 4. Maximum cell power density vs. cell temperature. E-TEK 20% Pt/C; Pt = 0.12 mg/cm^2.

an MEA at different temperatures. In the whole current density range, the performance increased with the cell temperature. The highest power densities achieved were 0.52, 0.60, 0.63, and 0.72 W/cm^2 at 35, 50, 60, and 75 °C, respectively. Such power densities were among the highest values ever achieved in PEM fuel cells with such a low Pt loading and operated using air (rather than pure oxygen) at ambient pressure. Also interestingly, the highest power density increased almost linearly with the cell temperature as illustrated in Fig. 4.

3.4. Performance versus Pt loading

Pt is a rare and expensive metal, hence reducing its loading without losing performance has always been a major goal. Fig. 5 shows how performance correlates with Pt loadings for electrodes made using 20% Pt/C. Large increases were observed when the loading was increased from 0.022 to 0.083 mg/cm^2. After 0.083 mg/cm^2, the change became much less, and a best performance was achieved at a loading of 0.138–0.253 mg/cm^2. When the loading was further increased,
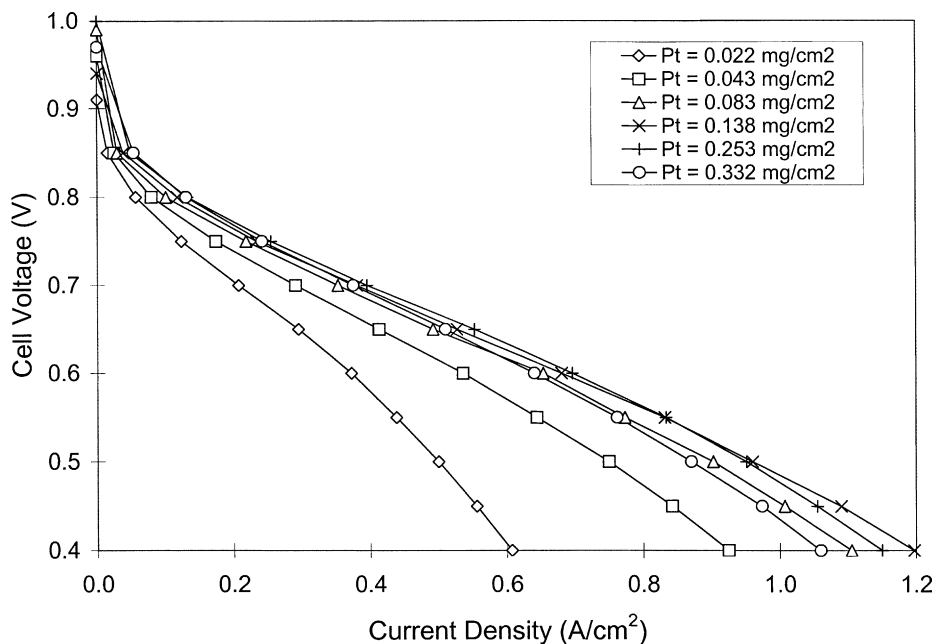

Fig. 5. Effect of Pt loading on performance for electrodes made using E-TEK 20% Pt/C, 35/45/45 °C.
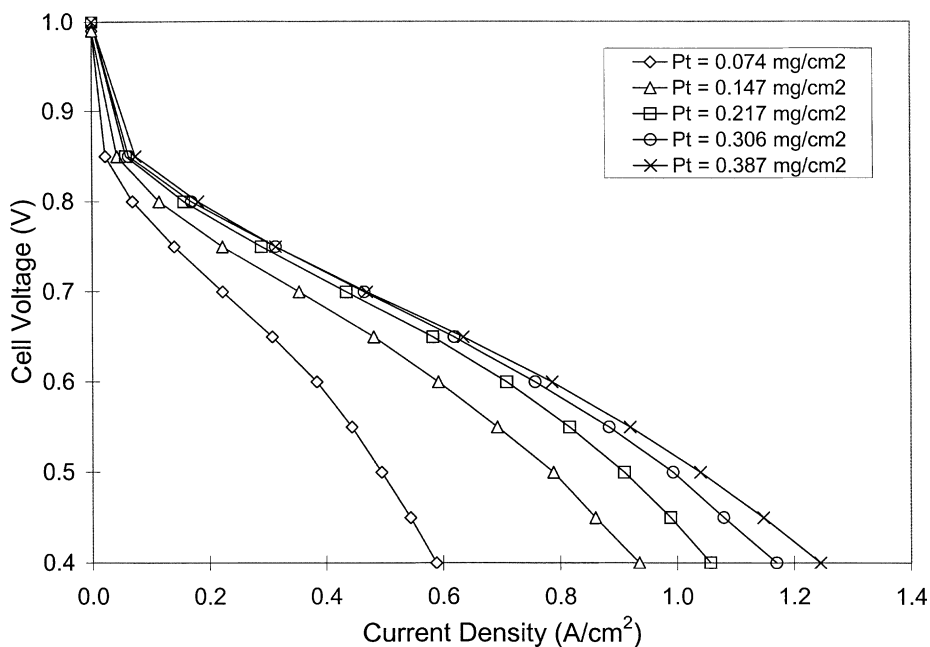
Fig. 6. Effect of Pt loading on performance for electrodes made using E-TEK 40% Pt/C, 35/45/45 °C.

the performance started to decline. Based on these results, an optimum Pt loading would be around 0.20 ± 0.05 mg/cm^2 when 20% Pt/C was used to make the electrode.

Fig. 6 shows the effect of Pt loading on performance for electrodes made using 40% Pt/C. Similarly, large increases were observed when the loading was increased from 0.074 to 0.217 mg/cm^2. After 0.217 mg/cm^2, the change became gradual, and a best performance seemed to be reached at a loading of 0.306–0.387 mg/cm^2. An optimum Pt loading would be around 0.35 ± 0.05 mg/cm^2.

It is not surprising that when 40% Pt/C is used, a higher Pt loading is needed to achieve the best performance than when 20% Pt/C is used, because the Pt particle size of the former is almost twice as large as that of the latter (3.9 nm versus 2.0 nm) [14]. Larger particle size corresponds to a smaller surface area (72 m^2/g for 40% Pt/C versus 112 m^2/g for 20% Pt/C) [14].

In order to compare the performance of 20 and 40% Pt/C side by side, the current density versus Pt loading at a cell voltage of 0.60 V for both catalysts is presented in Fig. 7.
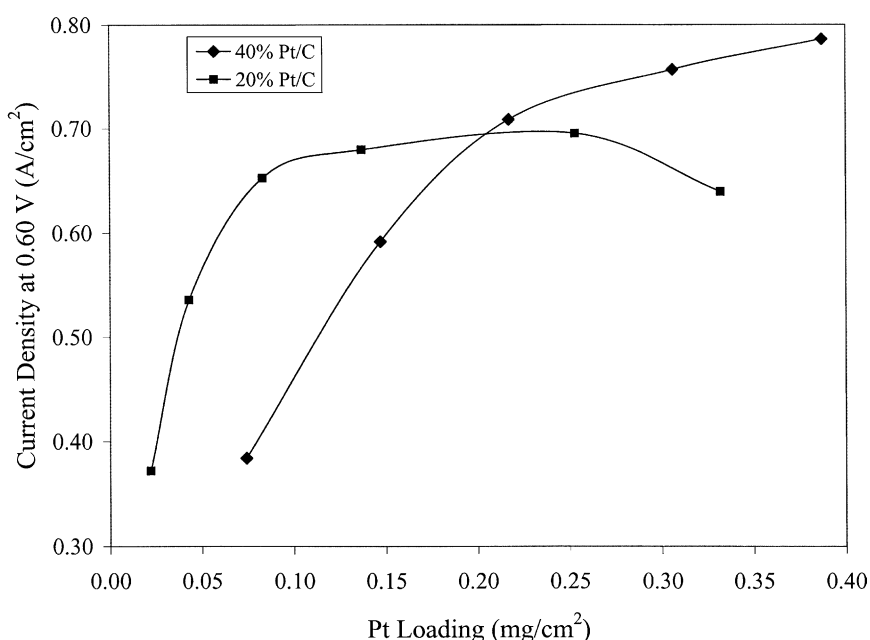

Fig. 7. Current density at 0.60 V vs. Pt loading for electrodes made using E-TEK 20 and 40% Pt/C, respectively, 35/45/45 °C.
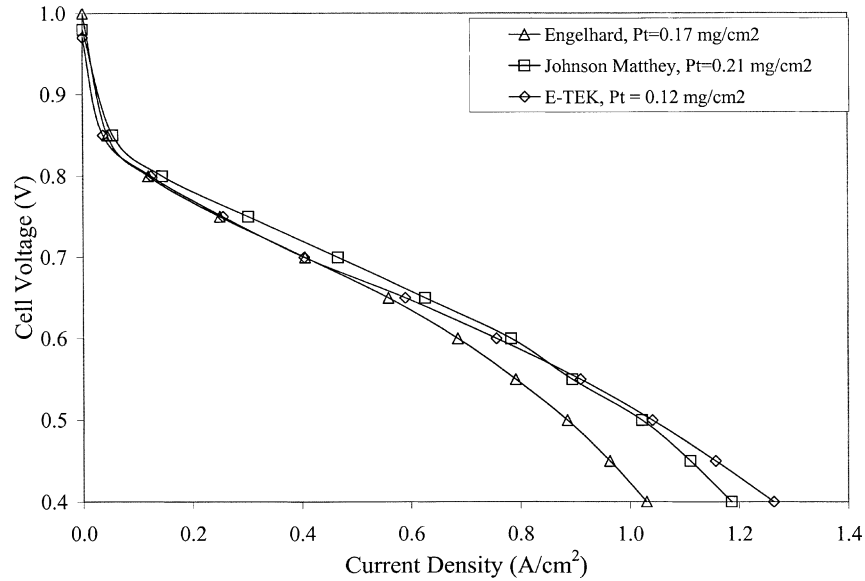
Fig. 8. Performance comparison among electrodes made using E-TEK, Johnson Matthey, and Engelhard 20% Pt/C, 35/45/45 °C.

It is interesting to notice that even with a double Pt loading, the optimum performance of 40% Pt/C is only slight better than that of 20% Pt/C. So, the use of 20% instead of 40% Pt/C could save as much as half of the catalyst while the performance only suffers slightly.

3.5. Performance of catalysts from other manufacturers

Supported catalysts (20% Pt/Vulcan XC-72R) from Engelhard and Johnson Matthey were also evaluated using the same mixing technique. Figs. 8 and 9 show that these catalysts have similar performance as E-TEK catalyst.

3.6. Performance versus Nafion/carbon sublayer

There was some interesting research indicating that adding a Nafion/carbon sublayer between the substrate and the catalyst layer could increase the performance [15]. In order to test if such a layer had a positive effect on ELAT, Nafion/carbon sublayers with Nafion contents ranging from 10 to 30% were applied to ELAT and the resulting gas diffusion media were evaluated. The carbon loadings in the Nafion/carbon layers were ca. 0.20 mg/cm^2, while the Pt loading in the catalyst layer was ranging from 0.33 to 0.40 mg/cm^2. The results shown in Fig. 8 indicate that such a layer has little effect on the performance of electrode using ELAT as the substrate.
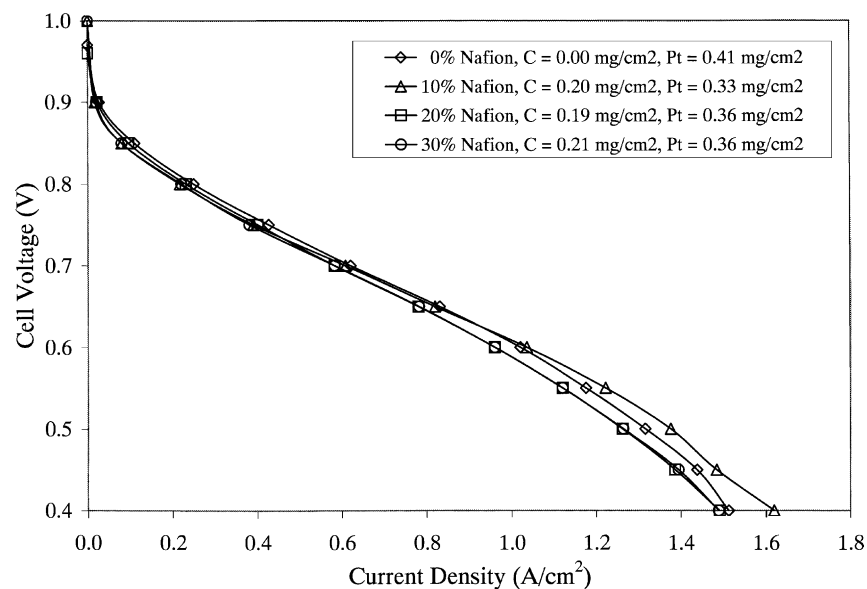

Fig. 9. Effect of Nafion/carbon sublayer on performance. Vulcan XC-72R was used for the Nafion/carbon layer; Engelhard 40% Pt/C was used for the catalyst layer, 35/45/45 °C.

4. Conclusions

A simple method of directly mixing carbon-supported catalysts with Nafion without adding any additional organic solvents was used to make electrodes for oxygen reduction reaction. These electrodes exhibited excellent performance. Using E-TEK 20% Pt/C, a Nafion content of 30% in the catalyst layer yielded the best performance. Power densities as high as 0.52, 0.60, 0.63, and 0.72 W/cm^2 were achieved at cell temperatures of 35, 50, 60, and 75 °C, respectively, for a cathode with a Pt loading of 0.12 mg/cm^2 and operated using air under ambient pressure. A maximum performance was achieved with Pt loadings of 0.20 ± 0.05 and 0.35 ± 0.05 mg/cm^2 for 20 and 40% Pt/C, respectively.

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