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CO-tolerance of low-loaded Pt/Ru anodes for PEM fuel cells

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Abstract

Anodes with various Pt/Ru loadings were prepared using three different anode catalysts: E-TEK 40% Pt-Ru/Vulcan XC-72 and Engelhard 40 and 50% Pt-Ru/C. These anodes were tested for their CO-tolerance at a cell temperature of 70 °C in the presence of 10 and 50 ppm CO, respectively. The performance declined with CO concentration for all the anodes. However, Engelhard catalysts showed better performance than E-TEK catalyst under our experimental conditions. A minimum Pt/Ru loading of 0.43, 0.22 and 0.30 mg/cm^2 was needed to achieve the maximum performance for E-TEK 40% Pt-Ru/C, Engelhard 40 and 50% Pt-Ru/C, respectively, when 10 ppm CO/70% H_2/30% CO_2 was used at a cell current density of 0.20 A/cm^2. Using 50 ppm CO/70% H_2/30% CO_2 and at a cell current density of 0.20 A/cm^2, a minimum Pt/Ru loading of 0.60, 0.32 and 0.36 mg/cm^2 was needed to achieve the highest performance for E-TEK 40% Pt-Ru/C, Engelhard 40 and 50% Pt-Ru/C, respectively.

Keywords: PEM fuel cells; CO-tolerance; E-TEK; Engelhard

1. Introduction

Anode poisoning by CO substantially lowers the performance of a proton exchange membrane (PEM) fuel cell. Mitigating such a poisoning effect has been an ongoing task challenging scientists and engineers in this field. One solution to mitigating the poisoning is to use alloyed catalysts such as Pt/Ru, Pt/Mo, Pt/Ru/Mo, Pt/Sn, Pt/Ru/WO_3 and Pd/Au, which exhibit improved CO-tolerance [1–12]. The improvement is due to either a lowered CO oxidation potential or a weakened adsorption of CO on these catalysts. This is the most convenient approach because it does not introduce any additional steps or hardware. It is quite effective to handle a reformate containing less than 10 ppm CO, but it is not adequate when the CO concentration is higher. In the presence of higher CO concentration, an additional step involving bleeding an oxidant into the anode compartment has been explored [13–17]. The bleeding oxidant, which can be air, oxygen, or hydrogen peroxide, chemically oxidizes CO to CO_2 and thus lowers its concentration. Caution must be taken in exercising this procedure to assure safe fuel cell operation. Furthermore, only about 1 out of 400 oxygen molecules participates in the oxidation of CO [17], and the remaining oxygen chemically combusts with hydrogen. The combustion reaction not only lowers the fuel efficiency, but might also accelerate the sintering of catalyst particles to lead to a performance decline with time. In addition, the chemical combustion might also create pinholes in the electrolyte membrane, which could result in cell failure.

Currently, Pt-Ru/C is the most popular CO-tolerant catalyst used in anodes for PEM fuel cells. The Pt/Ru loading in the catalyst layer determines the degree of CO-tolerance, and the optimal loading is also dependent on the fuel cell operation conditions such as current density, cell temperature, and CO concentration. Normally, higher current density, lower cell temperature, and higher CO concentration require a higher Pt/Ru loading. Recently, we found that even when all these conditions were the same, catalysts made by different manufacturers had different CO-tolerance. This article reports the relative CO-tolerance of E-TEK 40% Pt-Ru/Vulcan XC-72, and Engelhard 40 and 50% Pt-Ru/C.

2. Experimental

Catalyst mixtures were prepared by directly mixing a Pt-Ru/C catalyst with Nafion at a mass ratio of catalyst:Nafion = 70:30. All the carbon-supported Pt-Ru catalysts reported here had a Pt:Ru atomic ratio of 1:1. The carbon black in E-TEK 40% Pt-Ru/C was Vulcan XC-72,

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but it was not specified for Engelhard catalysts by the manufacturer. The mixtures were thoroughly mixed before they were applied onto Teflon-treated carbon-paper-type gas diffusion layers. The electrodes were dried at room temperature for 30 min, and then at 135 °C for another 30 min.

Membrane-electrode assemblies (MEAs) were made by hot-pressing electrodes onto Nafion 1135 membranes at 130 °C for 3 min. An electrode prepared as above was used as the anode. Another electrode with a Pt loading higher than 1.0 mg/cm^2 was used as the cathode. The purpose of using a high Pt-loading cathode was to minimize the effect of cathode on performance [18–19].

MEAs were tested using a 10 cm^2 single cell (Fuel Cell Technologies Inc., Albuquerque, New Mexico) at ambient pressure without oxidant bleeding. The cell was composed of a pair of graphite plates with serpentine flow-fields. Air was used as the oxidant, and pure H_2, or 10 ppm CO/70% H_2/30% CO_2, or 50 ppm CO/70% H_2/30% CO_2 was used as the fuel gas. The two CO-containing gases were prepared to contain 70% H_2 and 30% CO_2 in order to simulate the composition of a reformate stream from steam reforming. The reactants were humidified by passing them through stainless steel water bottles at the same temperature as the cell, which was 70 °C for all the tests. The stoichiometries of hydrogen, CO-containing gases, and air were controlled at 3.0, 2.0, and 2.5, respectively. The voltage (*V*)–current density (*I*) curves were collected using an HP 6050A load bank.

3. Results and discussion

3.1. E-TEK 40% Pt-Ru/Vulcan XC-72

Fig. 1 shows the *V–I* curves of an MEA whose anode was made using E-TEK 40% Pt-Ru/Vulcan XC-72 with a Pt/Ru loading of 0.60 mg/cm^2. The tests were performed sequentially by using pure H_2, 10 ppm CO/70% H_2/30% CO_2, 50 ppm CO/70% H_2/30% CO_2, and pure H_2. At a current density less than 0.05 A/cm^2, the electrode showed very similar performance with all these fuel gases, indicating that even in the presence of 50 ppm CO, the anode remains enough active catalyst site to generate this small current density without additional loss in activation overpotential. When the current density was larger than 0.05 A/cm^2, the performance declined with increase of CO concentration from 0 to 10 and to 50 ppm, and the higher the current density, the larger the decline. After the fuel gas was switched from 50 ppm CO/70% H_2/30% CO_2 back to pure H_2, the cell was first operated at a current density of 0.20 A/cm^2 for 60 min before the *V–I* curve was taken. During this process, it was observed that the cell voltage recovered quickly, and stabilized after about 20 min. But when the *V–I* curve was taken, the cell did not regain its initial performance as shown in Fig. 1, indicating that there was still some CO adsorbed.

Using pure H_2, the performance of MEAs with various anode Pt/Ru loadings was presented in Fig. 2. Little difference in performance was observed, indicating that a Pt/Ru loading of 0.19 mg/cm^2 was high enough to sustain efficient H_2 oxidation reaction. The slightly lower performance of the anode with the highest Pt/Ru loading (1.06 mg/cm^2) might be because of its higher ohmic resistance and higher mass transport limitation to reactants due to its greater thickness.

When 10 ppm CO/70% H_2/30% CO_2 was used, the electrode with a Pt/Ru loading of 0.19 mg/cm^2 had the lowest performance, but all the other electrodes with higher Pt/Ru loadings showed similar performance as shown in Fig. 3. This indicates that a Pt/Ru loading of 0.43 mg/cm^2 is high enough to tolerate 10 ppm CO.

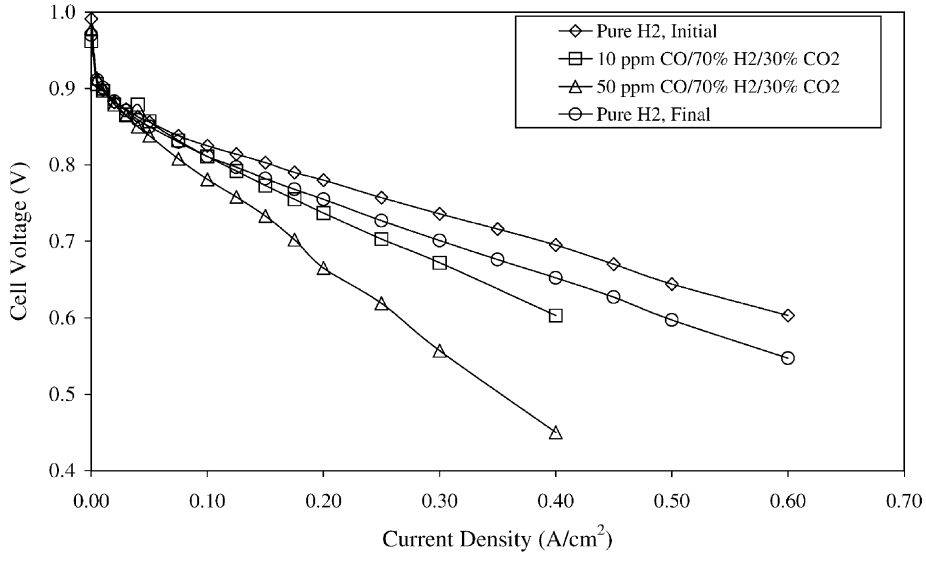

Fig. 1. Cell performance when the fuel was sequentially changed from pure H_2, to 10 ppm CO/70% H_2/30% CO_2, to 50 ppm CO/70% H_2/30% CO_2, and finally back to pure H_2. E-TEK 40% Pt-Ru/Vulcan XC-72; Pt-Ru = 0.60 mg/cm^2.

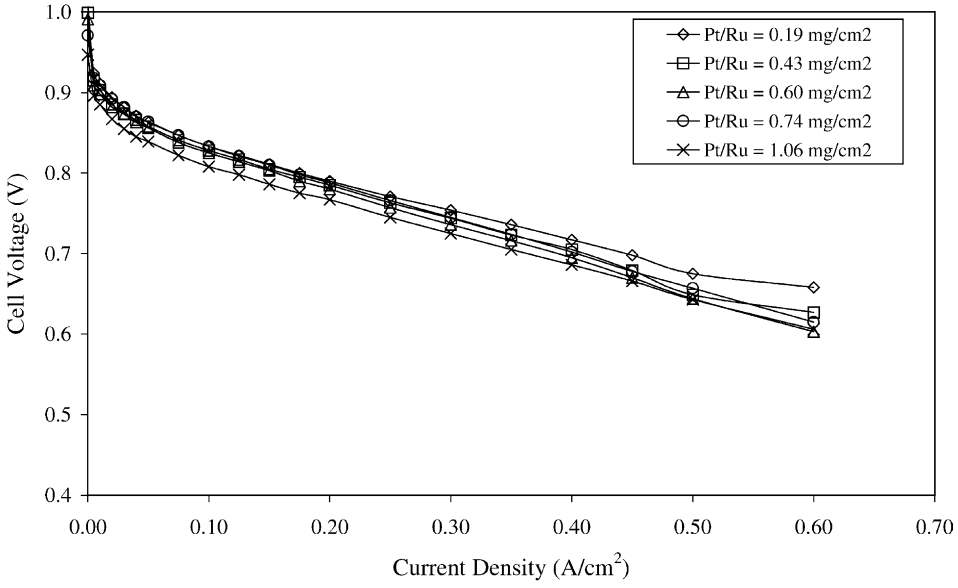

Fig. 2. Effect of Pt/Ru loading on performance when using pure H_2 as the fuel. E-TEK 40% Pt-Ru/Vulcan XC-72.

Fig. 4 shows the performance of those MEAs when 50 ppm CO/70% H_2/30% CO_2 was used. The cell voltage of the MEA with an anode Pt/Ru loading of 0.19 mg/cm^2 dropped continuously, so a meaningful *V–I* curve could not be obtained. The electrode with a Pt/Ru loading of 0.43 mg/cm^2 was inferior to those with higher Pt/Ru loadings. A Pt/Ru loading of 0.60 mg/cm^2 or higher was needed in order to achieve the maximum performance.

3.2. Engelhard 40% Pt-Ru/C

Fig. 5 shows the performance of an MEA with an anode Pt/Ru loading of 0.32 mg/cm^2 made using Engelhard 40% Pt-Ru/C. The fuel gas was sequentially changed from pure H_2 to 10 ppm CO/70% H_2/30% CO_2, to 50 ppm CO/70% H_2/30% CO_2, and finally back to pure H_2. Similar to that shown in Fig. 1, the performance declined with increasing CO concentration; and after the fuel gas was switched back to pure H_2, the performance did not recover completely. However, the performance declined much less than that of E-TEK 40%Pt/C in the presence of CO.

In both pure H_2 and 10 ppm CO/70% H_2/30% CO_2, all the anodes with Pt/Ru loading ranging from 0.22 to 0.83 mg/cm^2 showed similar performance, so their *V–I* curves under these conditions do not need to be plotted. However, Fig. 6

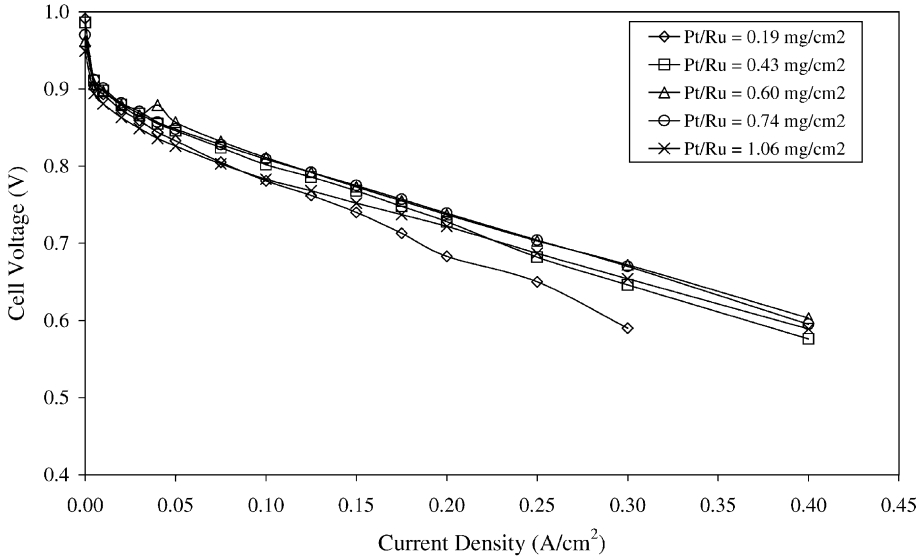

Fig. 3. Effect of Pt/Ru loading on performance when using 10 ppm CO/70% H_2/30% CO_2 as the fuel. E-TEK 40% Pt-Ru/Vulcan XC-72.

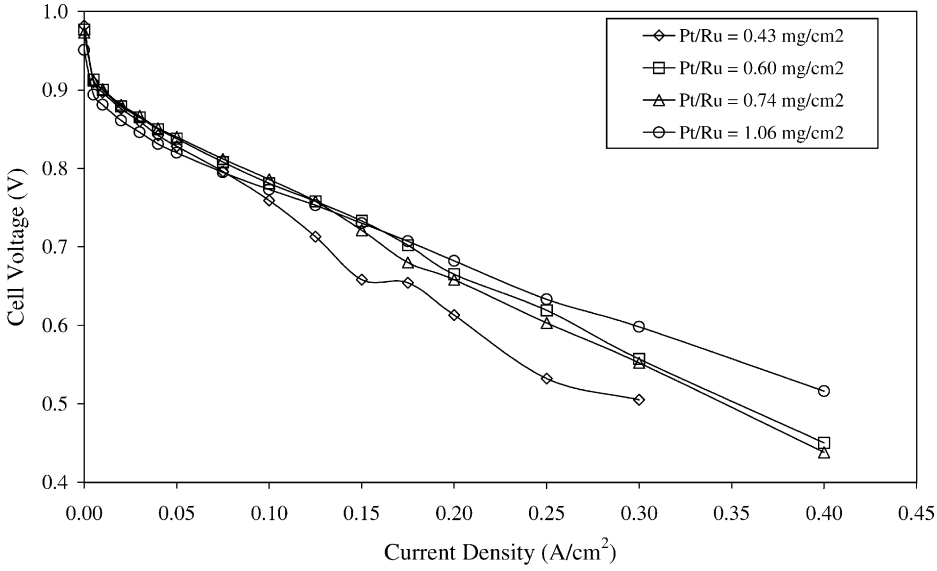

Fig. 4. Effect of Pt/Ru loading on performance when using 50 ppm CO/70% H_2/30% CO_2 as the fuel. E-TEK 40% Pt-Ru/Vulcan XC-72.

illustrates the performance of these MEAs in 50 ppm CO/70% H_2/30% CO_2. Clearly, when the Pt/Ru loading was 0.32 mg/cm^2 or higher, a maximum performance was achieved.

Fig. 7 shows how the cell voltage declined with time for these MEAs. With a Pt/Ru loading of 0.15 mg/cm^2, large decline was observed and the cell voltage finally oscillated around 0.64 V. The decline was sizably reduced when the Pt/Ru loading was increased to just 0.22 mg/cm^2. When the Pt/Ru loading was 0.32 mg/cm^2 or higher, a minimum performance decline was achieved.

When the anode fuel gas was switched to pure H_2 from 50 ppm CO/70% H_2/30% CO_2, the fuel cell performance recovered quickly, and within 20 min the cell voltage stabilized for all the MEAs, as shown in Fig. 8.

3.3. Engelhard 50% Pt-Ru/C

Fig. 9 shows the performance in various fuel gases of an MEA with an anode Pt/Ru loading of 0.20 mg/cm^2 made using Engelhard 50% Pt-Ru/C. The cell performance using 10 ppm CO/70% H_2/30% CO_2 was only slightly lower than

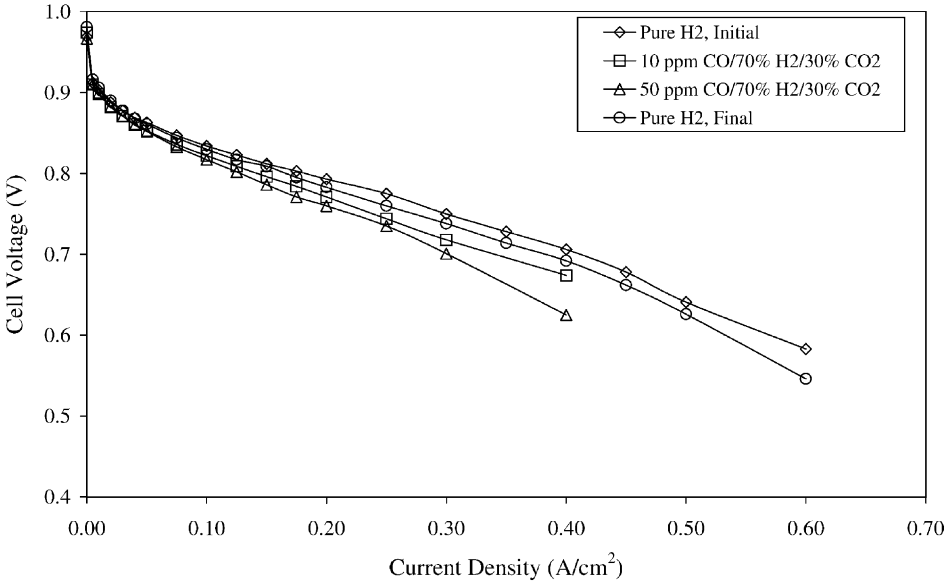

Fig. 5. Cell performance when the fuel was sequentially changed from pure H_2, to 10 ppm CO/70% H_2/30% CO_2, to 50 ppm CO/70% H_2/30% CO_2, and finally back to pure H_2. Engelhard 40% Pt-Ru/C; Pt-Ru = 0.32 mg/cm^2.

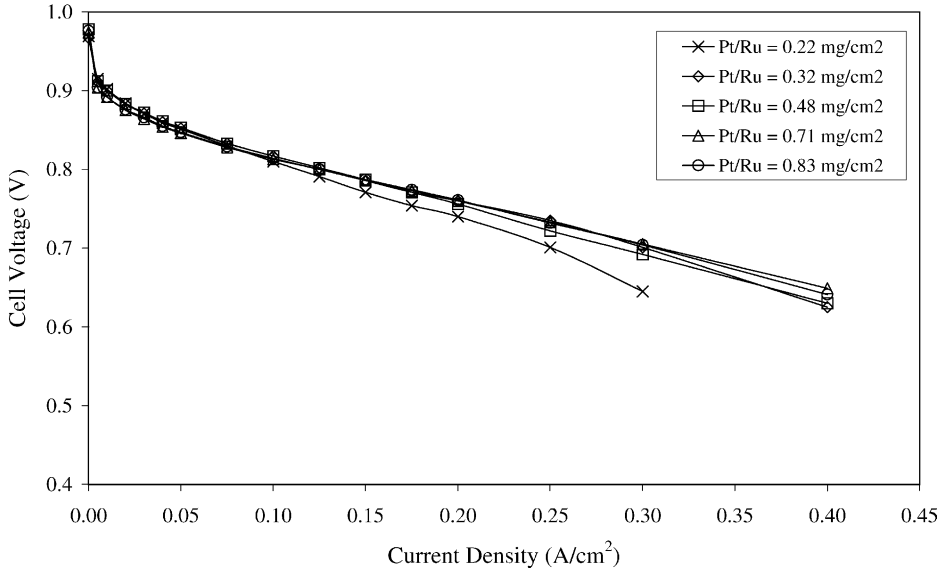

Fig. 6. Effect of Pt/Ru loading on performance when using 50 ppm CO/70% H_2/30% CO_2 as the fuel. Engelhard 40% Pt-Ru/C.

that using pure H_2, but the performance using 50 ppm CO/70% H_2/30% CO_2 was substantially lower, especially at higher current densities.

In the presence of 50 ppm CO/70% H_2/30% CO_2, the performance of four MEAs with various anode Pt/Ru loadings is shown in Fig. 10. Obviously, a loading of 0.20 mg/cm^2 was not sufficient. At a current density less than 0.15 A/cm^2, a loading of 0.36 mg/cm^2 was enough to achieve the maximum performance; but at higher current densities the performance increased with Pt/Ru loading.

Fig. 11 shows the performance decline of these MEAs with time in 50 ppm CO/70% H_2/30% CO_2. It can be seen that a large improvement was achieved when the loading was increased from 0.20 to 0.36 mg/cm^2, but further increase in loading resulted in only small increase.

The performance of these MEAs recovered quickly in pure H_2 as illustrated in Fig. 12. Within 20 min, all the cells reached a stabilized and similar value. For the anode with a Pt/Ru loading of 0.52 mg/cm^2, the H_2 flow rate was much higher than three times stoichiometry in the beginning. Within about 1 min that was spent to switch gas and to set up the cell to run at 0.20 A/cm^2, the cell had already recovered. When the stoichiometry was changed back to three times, the cell returned to its normal performance level.

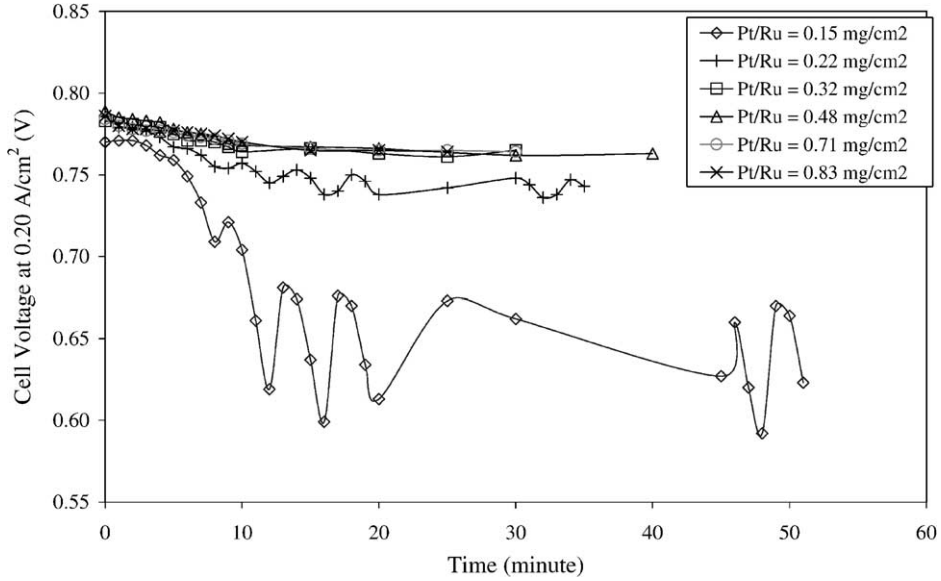

Fig. 7. Cell voltage change with time at a current density of 0.20 A/cm^2 when using 50 ppm CO/70% H_2/30% CO_2 as the fuel. Engelhard 40% Pt-Ru/C.

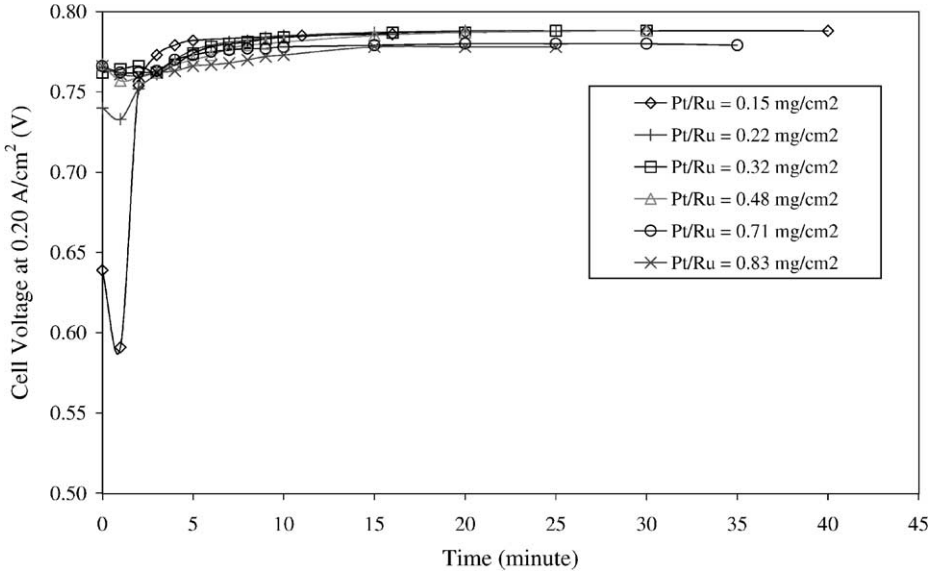

Fig. 8. Cell voltage recovery with time at a current density of 0.20 A/cm^2 after the fuel being switched to pure H_2 from 50 ppm CO/70% H_2/30% CO_2. Engelhard 40% Pt/C.

This test indicates that the cell recovers faster at higher H_2 flow rates.

3.4. Performance comparison

Fig. 13 presents cell voltage (at a current density of 0.2 A/cm^2) versus Pt/Ru loading for the three different catalysts when tested using 10 ppm CO/70% H_2/30% CO_2. E-TEK 40% Pt-Ru/Vulcan XC-72 showed the lowest performance, and a Pt/Ru loading between 0.43 and 0.74 mg/cm^2 gave the maximum performance. Engelhard 40 and 50% Pt-Ru/C both had higher performance. For its 40% Pt-Ru/C, a Pt/Ru loading of 0.22 mg/cm^2 or higher was required to achieve the maximum performance. For its 50% Pt-Ru/C, the Pt/Ru loading needed to be 0.36 mg/cm^2 or higher to achieve the maximum performance.

Fig. 14 compares these catalysts at a current density of 0.2 A/cm^2 when 50 ppm CO/70% H_2/30% CO_2 was used. E-TEK 40% Pt-Ru/Vulcan XC-72 again showed the lowest performance, and a Pt/Ru loading of 0.60 mg/cm^2 or higher was needed to achieve the maximum performance. For Engelhard 40% Pt-Ru/C, a large increase was observed when the Pt/Ru loading was increased from 0.15 to 0.22 mg/cm^2, and the maximum performance was achieved

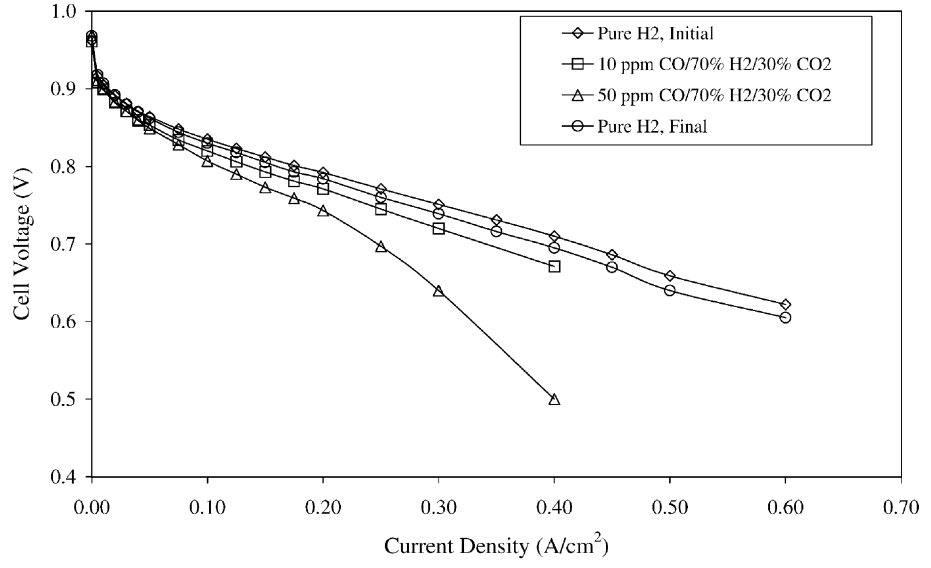

Fig. 9. Cell performance when the fuel was sequentially changed from pure H_2 to 10 ppm CO/70% H_2/30% CO_2, to 50 ppm CO/70% H_2/30% CO_2 and finally back to pure H_2. Engelhard 50% Pt-Ru/C; Pt-Ru = 0.20 mg/cm^2.

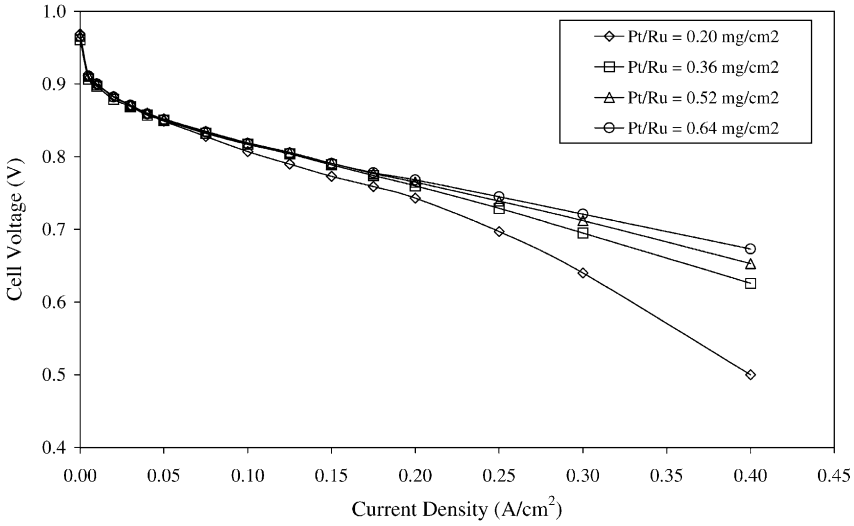

Fig. 10. Effect of Pt/Ru loading on performance when using 50 ppm CO/70% H_2/30% CO_2 as the fuel. Engelhard 50% Pt-Ru/C.

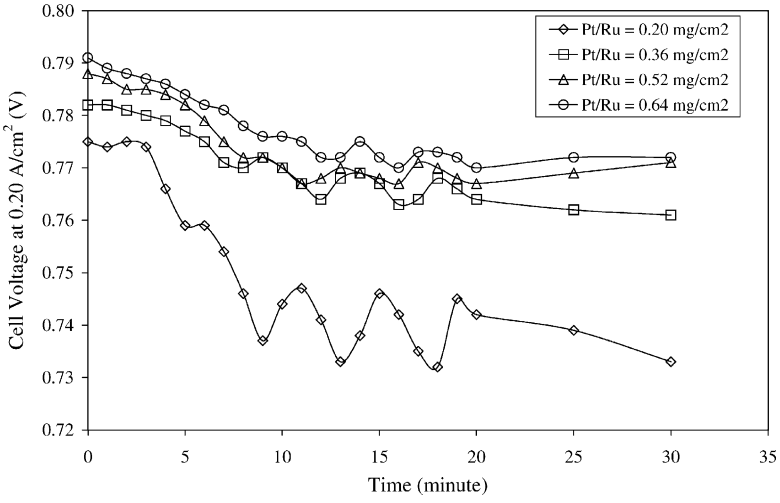

Fig. 11. Cell voltage change with time at a current density of 0.20 A/cm^2 when using 50 ppm CO/70% H_2/30% CO_2 as the fuel. Engelhard 50% Pt-Ru/C.

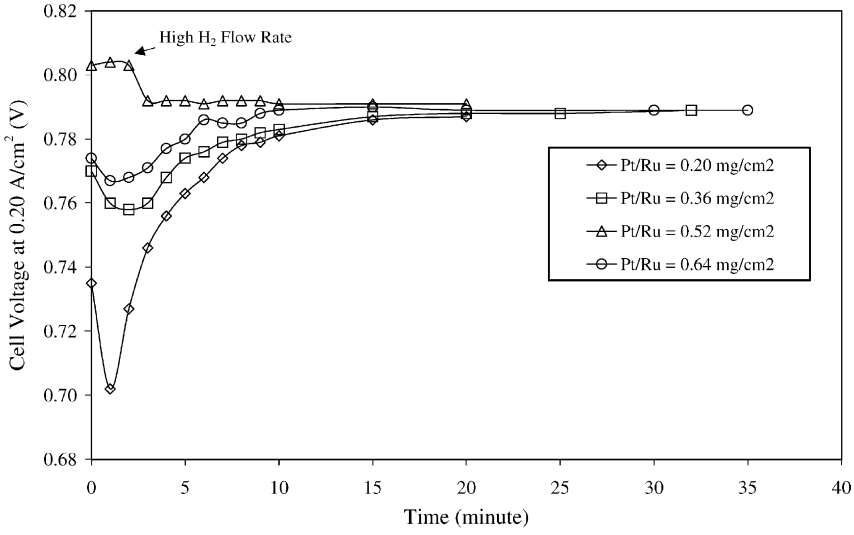

Fig. 12. Cell voltage recovery with time at a current density of 0.20 A/cm^2 after the fuel being switched to pure H_2 from 50 ppm CO/70% H_2/30% CO_2. Engelhard 50% Pt/C.

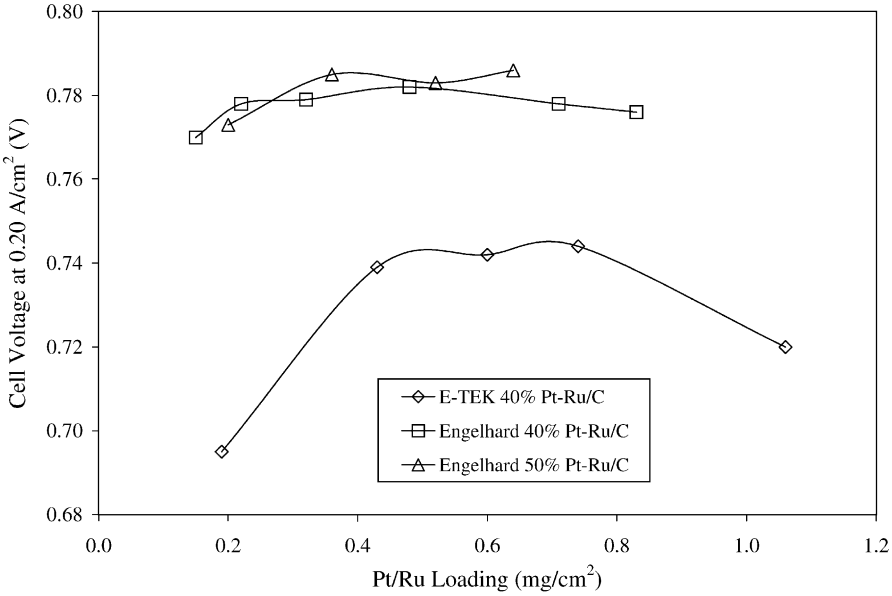

Fig. 13. Cell voltage at 0.2 A/cm^2 vs. Pt/Ru loading for E-TEK and Engelhard Pt-Ru/C when using 10 ppm CO/70% H_2/30% CO_2 as the fuel.

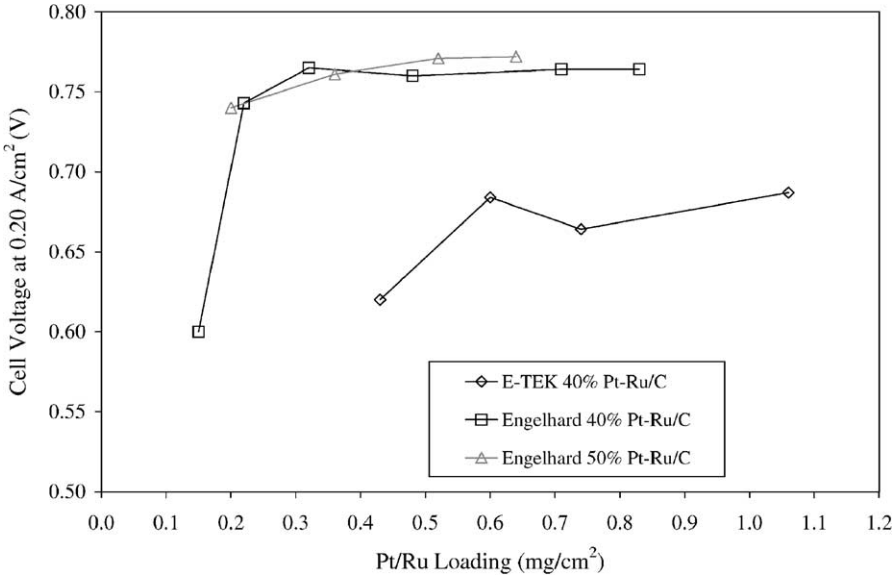

Fig. 14. Cell voltage at 0.2 A/cm^2 vs. Pt/Ru loading for E-TEK and Engelhard Pt-Ru/C when using 50 ppm CO/70% H_2/30% CO_2 as the fuel.

at a Pt/Ru loading of 0.32 mg/cm^2 or higher. For Engelhard 50% Pt-Ru/C, a Pt/Ru loading of 0.36 mg/cm^2 or higher was needed to achieve the maximum performance.

E-TEK Pt-Ru/Vulcan XC-72 catalyst had an average Pt-Ru crystallite particle size of 2.0–4.0 nm, while Engelhard carbon-supported Pt-Ru/C had an average Pt-Ru crystallite size of 3.5–4.5 nm. Hence, crystallite size and thus the related surface area did not explain the performance difference. The carbon support in E-TEK catalyst was Vulcan XC-72, but Engelhard catalysts listed the carbon support only as a ''carbon black'' with no further specifications. Due to the lack of this information, it is not possible for us to speculate why these catalysts perform differently. In addition, although E-TEK catalysts performed worse using our catalyst layer formulation and procedure, this might not be the case when a different preparation method was used.

4. Conclusions

The CO-tolerance of anodes with various Pt/Ru loadings made using both E-TEK 40% Pt-Ru/Vulcan XC-72 and Engelhard 40 and 50% Pt-Ru/C was studied. Engelhard

catalysts showed better CO-tolerance under our experimental conditions. Using 10 ppm CO/70% H_2/30% CO_2 and at a cell current density of 0.20 A/cm^2, a minimum Pt/Ru loading of 0.43, 0.22 and 0.30 mg/cm^2 was needed to achieve the maximum performance for E-TEK 40% Pt-Ru/Vulcan XC-72, Engelhard 40 and 50% Pt-Ru/C, respectively. Using 50 ppm CO/70% H_2/30% CO_2 and at a cell current density of 0.20 A/cm^2, a minimum Pt/Ru loading of 0.60, 0.32 and 0.36 mg/cm^2 was needed to achieve the maximum performance for E-TEK 40% Pt-Ru/C, Engelhard 40 and 50% Pt-Ru/C, respectively.

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