High performance carbon-supported catalysts for fuel cells via phosphonation

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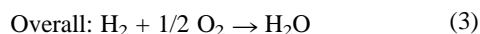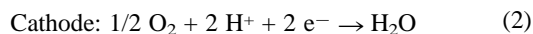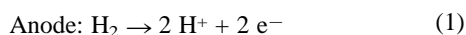*H Power Corporation, 60 Montgomery Street, Belleville, New Jersey 07109, USA.*
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Carbon-supported catalysts were phosphonated using 2-aminoethylphosphonic acid, and the resulting catalysts with largely enhanced proton conductivity performed substantially better than the untreated counterparts in proton-exchange membrane fuel cells.

Noble metals such as Pt and its alloys that are deposited on supports such as carbon particles are normally used to catalyze the electrochemical reactions in a proton-exchange membrane (PEM) fuel cell. Since the hydrogen oxidation reaction (1) and the oxygen reduction reaction (2) involve both electrons and protons, the catalyst layers have to be configured to transport both of them.

$$\text{Anode: } H_2 \rightarrow 2\,H^+ + 2\,e^- \qquad (1)$$

$$\text{Cathode: } 1/2\,O_2 + 2\,H^+ + 2\,e^- \rightarrow H_2O \qquad (2)$$

$$\text{Overall: } H_2 + 1/2\,O_2 \rightarrow H_2O \qquad (3)$$

The electronic path can be established by the catalyst phase itself, and the proton continuity is normally achieved by incorporating a proton conductor such as Nafion, a perfluoronated and sulfonated ionomer, into the catalyst layer.[1–4] However, since the reactions can only occur at the catalyst/Nafion/reactant three-phase regions, and the extent of such regions is obviously very limited in a catalyst layer, a large portion of the expensive noble metal catalyst is unavoidably wasted.[5]
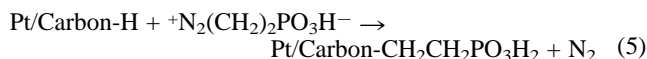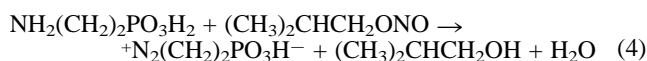
It has been envisioned that if the carbon support can be made to conduct both electrons and protons, the catalyst utilization will be largely increased. One method to make carbon particle conduct protons is to link some acidic groups onto its surface. Carboxylic acid groups were created onto the surface of carbon catalyst-support particles using hot nitric acid by Jia et al.[6] The resulting catalyst gained increased water wettability and proton conductivity, leading to an enhanced electrode performance. However, since carboxylic acid is a weak acid and a poor proton conductor, the increased performance was very limited. Easton et al attached sulfonated silane onto the surface of carbon support and achieved an optimal fuel cell performance when only 10% Nafion (by weight) was mixed into the catalyst layer, whereas 30% Nafion was needed to achieve the best performance for the unsulfonated counterpart.[7] However, the best performance of the sulfonated-silane-treated catalyst was not as good as that of the untreated counterpart.

We report here a novel and effective method to link alkylphosphonic acid groups onto the surface of carbon particles functioning as catalyst supports. The resulting phosphonated catalyst not only needs less Nafion within the catalyst layer, but also performs better than the unsulfonated counterpart.

Carbon-supported catalysts were phosphonated using 2-aminoethylphosphonic acid ($H_2N(CH_2)_nPO_3H_2$, $n = 2$) according to the following procedure: After a predetermined amount of 2-aminoethylphosponic acid was dissolved in 40 ml of water under stirring and heating, 5 grams of E-TEK 20% Pt/Vulcan XC-72 catalyst was added. The mixture was stirred for a few minutes and then cooled down to room temperature, followed by the addition of 6 mmol of isobutyl nitrite. After being stirred

for 1 hour the mixture was filtered. The solid product was washed with water and acetone and then dried under vacuum.

Isobutyl nitrite reacts with aminoethylphosphonic acid to form a diazonium inner salt [reaction (4)], which reacts in situ with carbon particles through its surface C–H bonds[8] to have $-CH_2CH_2PO_3H_2$ linked onto carbon [reaction (5)]. The diazonium salt may undergo some side reactions such as coupling and hydrolysis, but all the side products and unbonded organic residues are washed out during filtration.

$$NH_2(CH_2)_2PO_3H_2 + (CH_3)_2CHCH_2ONO \rightarrow$$
$$^+N_2(CH_2)_2PO_3H^- + (CH_3)_2CHCH_2OH + H_2O \quad (4)$$

$$Pt/Carbon\text{-}H + {}^+N_2(CH_2)_2PO_3H^- \rightarrow$$
$$Pt/Carbon\text{-}CH_2CH_2PO_3H_2 + N_2 \quad (5)$$

Fuel cell electrodes were prepared by applying a mixture of Nafion and carbon-supported catalyst (either phosphonated or unphosphonated) onto carbon-paper type gas diffusion medium. The resulting electrode was then hot-pressed as a cathode onto Nafion 112 membrane with a standard anode to form a membrane-electrode assembly (MEA). The MEA was tested in a homemade 10 cm^2 single cell with pure H_2 as the fuel, and air as the oxidant under ambient pressure. Since the anode has a high Pt loading (> 1 mg cm^{-2}) and hydrogen oxidation reaction is far more active than the oxygen reduction reaction, the performance of the cathode that was under investigation determines the overall cell performance.

The amount of $-CH_2CH_2PO_3H_2$ groups that are linked onto carbon is determined by the amount of 2-aminoethylphosphonic acid used. A larger amount of $-CH_2CH_2PO_3H_2$ will result in higher proton conductivity at the surface of carbon, and thus lead to a higher catalyst utilization and higher fuel cell performance. However, if the amount of $-CH_2CH_2PO_3H_2$ is too high, it will cause local accumulation of liquid water to flood the catalyst surface, which will result in lower fuel cell performance. In addition, the introduction of $-CH_2CH_2PO_3H_2$ may slightly reduce the electronic conductivity at the carbon surface. The optimal amount of 2-aminoethylphosphonic acid must be determined experimentally. Figure 1 shows the current density at a cell voltage of 0.5 V for several electrodes made using 20% Pt/Vulcan XC-72 treated with various amounts of 2-aminoe-
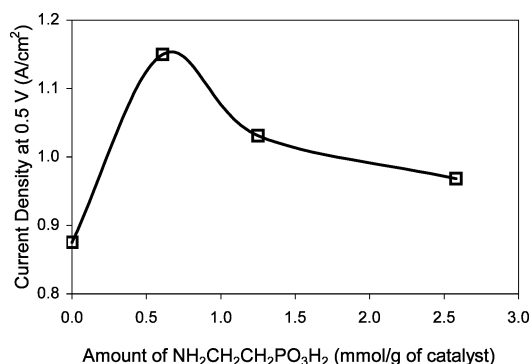

Fig. 1 Effect of the amount of 2-aminoethylphosphonic acid used to treat E-TEK 20% Pt/Vulcan XC-72 on fuel cell performance. Cell temperature = 35 °C; Pt loading = 0.3 mg cm^{-2}; Nafion content = 17.5%.
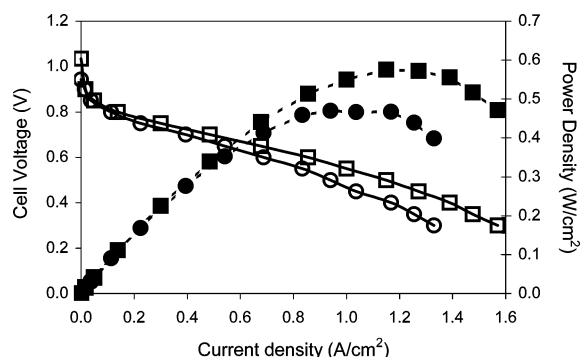
thylphosphonic acid. It can be seen that the optimal amount of 2-aminoethylphosphonic acid to phosphonate 20% Pt/Vulcan XC-72 is about 0.6 mmol per gram of catalyst.

Nafion is still needed in the electrode that uses phosphonated catalysts for at least two reasons. First, Nafion functions as a binder to join Pt/C particles together. Second, Nafion facilitates proton transfer among Pt/C particles. However, too much Nafion would reduce fuel cell performance by causing flooding and by decreasing porosity and electronic conductance within the catalyst layer. Figure 2 shows that the optimal Nafion content within a catalyst layer made using phosphonated 20% Pt/Vulcan XC-72 was about 20%. For the untreated counterpart the Nafion content needs to be as high as 30% to give the best performance.[7] Since the phosphonated catalyst contains ethylphosphonic acid groups on the surface of carbon, it is not surprising that it needs less Nafion in the catalyst layer to achieve the highest performance. It is expected that the proton transfer mainly follows a hopping (Grotthus) mechanism under the fuel cell operating condition.

The most exciting result is that the best performance of electrodes made using phosphonated Pt/Vulcan XC-72 is much better than that made using the unphosphonated counterpart, as shown in Fig. 3. Even with 10% less Nafion, the phosphonated catalyst has higher performance over the entire current density region. The highest power densities achieved by phosphonated and unphosphonated catalysts are 0.57 and 0.47 W cm^{-2}, respectively, the former being about 20% higher than the latter. Clearly, the introduction of ethylphosphonic acid groups onto
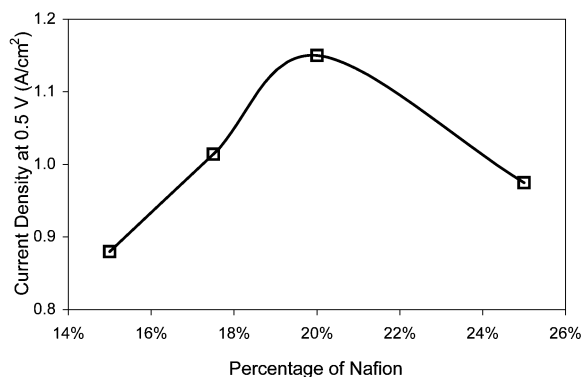
Fig. 3 Best performance of phosphonated (■,□) and unphosphonated (●,○) 20% Pt/Vulcan XC-72. Catalyst layers contained 20 and 30% Nafion for the phosphonated and unphosphonated catalysts, respectively. Empty symbols: cell voltage; Solid symbols: power density; Cell temperature = 35 °C; Pt loading = 0.3 mg cm^{-2}.

the catalyst surface dramatically increases catalyst utilization. The combination of 10% Nafion reduction and 20% performance increase will decrease the cost of a fuel cell for at least 20%.

Aminomethylphosphonic acid and 1-aminopropylphosphonic acid were also used to treat E-TEK 20% Pt/Vulcan XC-72. They also lowered the optimal Nafion content within the catalyst layers to about 20%, but the results were not as good as with 1-aminoethylphosphonic acid. The effect of the length of linked acidic groups on catalyst performance is under investigation. Groups with long chains may hinder the transport of reactants to the reaction sites.

Notes and references

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Fig. 2 Effect of Nafion content in the catalyst layer on the performance of phosphonated 20% Pt/Vulcan XC-72. Phosphonation was done using 0.6 mmol 1-aminoethylphosphonic acid per gram of catalyst. Cell temperature = 35 °C; Pt loading = 0.3 mg cm^{-2}.