Low Loading Pt Cathode Catalysts for Direct Methanol Fuel Cell Derived from the Particle Size Effect

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The direct methanol fuel cell (DMFC) has attracted considerable attention in mobile power applications because of its advantage of being easy to handle and having no necessity for a complex reformer unit in comparison to the H_2-fed polymer electrolyte membrane fuel cell (PEMFC). Today, one of the biggest hurdles for DMFC to reach commercialization is still the requisite of a significant amount of platinum catalysts to achieve an acceptable power density. Usually, a Pt loading of 4−8 mg/cm^2 is used at the cathode of DMFC, in order to increase the oxygen reduction activity and reduce the power loss caused by the oxidation of the methanol arising from crossover. Recent results have shown that with sputtered Pt cathode catalysts, the metal loading in PEMFC can be reduced to <0.1 mg/cm^2 with the cell still being able to produce a significant power density.[1] However, although much effort has been dedicated to the reduction of cathode metal loading in PEMFC, less attention has been paid to DMFC.

It is necessary to have in-depth knowledge about the correlation between catalyst morphology and electroactivity, e.g., particle size effects, which is essential for developing the high-activity catalyst and reducing the Pt loading. So far, most research reports about the oxygen reduction reaction (ORR) activities have been done in half-cell configurations with Pt particles larger than 2 nm, and the existence of the particle size effect for ORR has been discussed quite controversially. Although Watanabe et al. claimed that the Pt interparticle distances played a more important role than the crystallite size itself,[2] most groups found size-dependent ORR activities. For instance, Kinoshita et al. argued that the ORR activities were essentially related to the relative fraction of Pt (111) and (100) faces on catalyst sufaces, and no effect from the interparticle distances was observed.[3] On the other hand, Takasu et al. have attributed the origin of particle size effects in the ORR to the stronger adsorption of oxygen on smaller Pt particles.[4] A similar conclusion was drawn from *in situ* XAS studies by Mukerjee et al.[5] They observed a decrease in ORR specific activities when the Pt nanoparticles were smaller than 5 nm, which was explained by a strong adsorption of OH. Mayrhofer et al. also found a stronger adsorption of OH on small-sized particles in perchloric acid electrolyte.[6] On the contrary, Maillard et al. reported an increase in the ORR mass activities when the Pt particle size decreases from 4.6 to 2.3 nm in a methanol-containing perchloric acid electrolyte, but they found that the ORR mass activities were rather independent of size (from 2.3 to 3.5 nm) in a methanol-free electrolyte.[7] Very recently, Watanabe and Wieckowski studied the ORR activities of a series of carbon-supported Pt nanoparticle electrocatalysts with average diameters of 1.6, 2.6, and 4.8 nm. The results showed that ORR rate constants did not demonstrate any particle size dependence.[8]

The impetus of this work is to investigate the single-cell performance of Pt cathode catalysts of different sizes, with a main emphasis on particles smaller than 2 nm. We are attempting to disclose the particle size effect in order to develop an improved catalyst for a significant reduction of the metal loading. Most recently, we introduced a novel approach for the preparation of small Pt clusters.[9] In the present work, this method was further explored for the preparation of series Pt nanoparticles with different sizes (d_{Pt} = 0.8, 1.1, 1.4, 1.8, and 3.2 nm). Because these catalysts were prepared according to the same protocol, the influences that arise from the different preparative methods can be excluded.

The Pt colloids were prepared by decomposing $(CH_3)_2$-Pt(cod) in the presence of Al(oct)$_3$ in toluene (cod = 1,5-cyclooctadiene, oct = octyl) (see Scheme 1). A typical procedure for the preparation of Pt colloid at 0.8 ± 0.1 nm was described in a previous work.[9] After Al(oct)$_3$ was introduced into the $(CH_3)_2$Pt(cod) solution in toluene, the reaction mixture immediately changed from colorless to brown. NMR investigations reveal that immediately after mixing, an extensive ligand exchange between Pt-methyl and Al-octyl occurs, followed by β-H elimination and reductive elimination of octene and octane from platinum. This leads to the dissociation of cod from platinum and the subsequent nanoparticle formation.

By tuning the ratio of Al to Pt and the reaction temperature, as shown in Figure 1, four particle sizes were obtained at 0.8 ± 0.1 nm (Al/Pt = 10, 25 °C), 1.1 ± 0.2 nm (Al/Pt = 4, 25 °C), 1.4 ± 0.3 nm (Al/Pt = 4, 60 °C), and 1.8 ± 0.2 nm (Al/Pt = 2, 25 °C), respectively.

The supported Pt catalysts were prepared by introducing the as-synthesized nanoparticles into a Vulcan XC-72R

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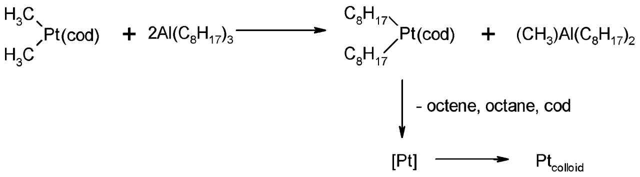
Scheme 1. Decomposition of $(CH_3)_2Pt(cod)$



suspension in toluene, stirring for 2 days, drying under vacuum, washing with NaOH aqueous solution, and finally cleaning with copious amount of water/acetone. The treatment with NaOH solution is necessary to remove the Al residue left on the Pt surfaces. Energy-dispersive X-ray (EDX) analysis revealed that after the leaching process, the Al content on all the samples are less than 0.2 wt %. The as-prepared samples are listed in Table 1. The sample designation is according to the particle size and final Pt loading on membrane electrode assembly (MEA). For example, Pt08-001 denotes the Pt catalyst with an average diameter of 0.8 nm and a metal loading of 0.01 mg/cm^2 on the electrode.

The sample Pt32-120 (3.2 nm) was prepared by adapting the so-called seed-growth method,[10] wherein the final particle size is determined by the size of the seeds and the molar ratio of ionic metal to metal seeds. Herein, the Pt nanoparticle with an average diameter of 0.8 nm was used as the seed, and the $(CH_3)_2Pt(cod)$ was reduced under hydrogen in the presence of Vulcan. According to the equation suggested by Turkevich,[11] the amount of $(CH_3)_2Pt(cod)$ and Pt colloid utilized was estimated to achieve a particle size of 3.0 nm. TEM images revealed that a supported catalyst with an average diameter of 3.2 nm was obtained, which is in good agreement with the calculation (see the Supporting Information).

Catalyst inks were prepared by mixing the supported Pt, water, and Nafion ionomer solution in an ultrasonic bath for 15 min, followed by stirring for 2 days. The weight ratio of Nafion to catalyst is 30/70. The inks were then painted on Toray carbon paper (Teflon treated) with different loadings. After electrodes were fully dried, Nafion 112 and electrodes were hot-pressed at 130 °C and 100 kgf/cm^2 for 3 min. The membrane electrode assembly (MEA) was then placed in a 5 cm^2 single cell (Electrochem, Inc.) for the DMFC activity examination. The single cell was first conditioned with 1.0 M MeOH and oxygen at 70 °C by running it galvanostatically under 20 mA and 100 mA each for 2 h. The cell was then operated at 90 °C with 1.0 M MeOH at 2 mL/min in the anode side and ambient pressure O_2 at 200 sccm in the cathode side. The polarization curves and impedance spectra were recorded using a Zahner IM6 impedance analyzer.

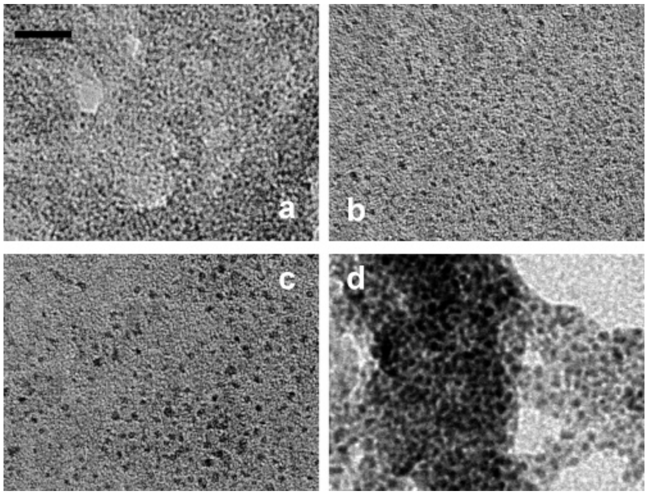


Figure 1. TEM images of Pt colloids prepared at different conditions: (a) 0.8 ± 0.1 nm; (b) 1.1 ± 0.2 nm; (c) 1.4 ± 0.3 nm; (d) 1.8 ± 0.2 nm. TEM measurements were performed on a Hitachi HF 2000 instrument operating at 200 kV. Scale bar: 10 nm.

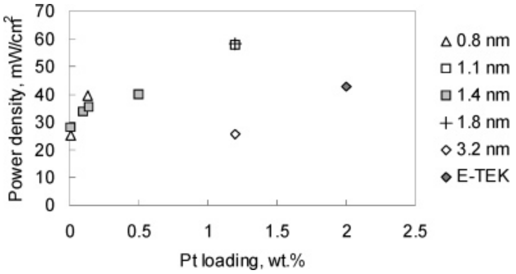


Figure 2. Power densities of different catalysts vs Pt loading.

In all the single-cell measurements, commercially available E-TEK PtRu/C 30 wt % was used as the anode catalyst with a noble metal loading of 2 mg/cm^2. To ascertain that the anode side is identical for different measurements and the comparison among the cathode catalysts was not affected by the anode performance, the impedance data of the anode side were recorded by running the cell with MeOH at the anode and H_2 instead of O_2 at the cathode according to the Mueller method.[12] The cathode impedance data can be extracted from the fuel cell impedance. Furthermore, considering that all the cathode catalysts in this work were prepared by an Al-organic approach, the comparison of the catalysts with different loading and particle size are plausible.

The electrochemical results of different catalysts are summarized in Table 1 and Figure 2. One can see that both samples Pt11-120 (1.1 nm) and Pt18-120 (1.8 nm) show better performance than the commercial E-TEK catalyst (Pt30-200, 3.0 nm), reflected by approximately 40% higher peak power densities but a 40% lower metal loading. The mass activity of E-TEK catalyst is only half that of the other two samples. Sample Pt14-050 (1.4 nm) shows comparable performance to the E-TEK one, but with a three-times-reduced Pt loading. Especially, with a 0.01 mg/cm^2 Pt loading (200 times lower than that of E-TEK catalyst), samples Pt08-001 and Pt14-001 already demonstrate 59 and 67% of E-TEK catalyst power densities. On the other hand, sample Pt32-120 with an average particle size of 3.2 nm showed identical mass activity as the E-TEK one. Therefore, these results indicate that smaller-sized particles give a higher performance when applied as the cathode catalysts in DMFC. Watanabe et al. recently suggested that there is a negligible difference in the surface electronic properties of Pt/C catalysts ranging from 1 to 5 nm, and accordingly, the ORR activities are not affected by the differences in particle size.[8] Therefore, one

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Table 1. Supported Pt Catalysts Used for the DMFC

sample	synthesis	average size (nm)	Pt/C (wt %)	loading (mg of Pt/cm^2)	power density (mW/cm^2)	mass activity (W/g)
Pt08-001	Al/Pt = 10	0.8 ± 0.1	0.1	0.01	25.1	2510.0
Pt08-013			2.0	0.13	39.5	303.8
Pt11-120	Al/Pt = 4	1.1 ± 0.2	18	1.20	57.8	48.2
Pt14-001	Al/Pt = 4	1.4 ± 0.3	0.1	0.01	28.1	2810.0
Pt14-010			1.0	0.10	33.8	338.0
Pt14-014			1.0	0.14	35.6	254.2
Pt14-050			5.0	0.50	40.0	80.0
Pt18-120	Al/Pt = 2	1.8 ± 0.2	20	1.20	58.3	48.6
Pt32-120	seeding method	3.2 ± 0.5	13	1.20	25.5	21.2
Pt32-023			2.3	0.23	0.2	0.7
Pt30- 200	E-TEK, Pt	3.0 ± 0.5	20	2.00	42.6	21.3

interpretation for our observation might be the higher dispersion of the small Pt particles in the present study. On the other hand, we have observed that Pt nanoparticles with sizes below 2 nm demonstrated very low methanol oxidation activities (see the Supporting Informaiton), which might reduce the voltage loss arising from the mixing potential at the cathode side. Thus, a higher DMFC performance could be expected.

The long-term performance of catalyst Pt14-050 in DMFC was examined to explore the stability of the small-sized Pt catalysts. The results of a 55 h durability test at 100 mA/cm^2 and 90 °C are shown in Figure 3, with a degradation rate of 1.1 mV/h. One can see that the voltage loss mostly took place in the first several hours and the decay then became insignificant, with a degradtion rate of 0.3 mV/h after 10 h of operation. As seen in Figure 3, a full recovery of the voltage loss was observed when the durability test was restarted, which is in accordance to the findings by Shukla and his co-workers.[13]

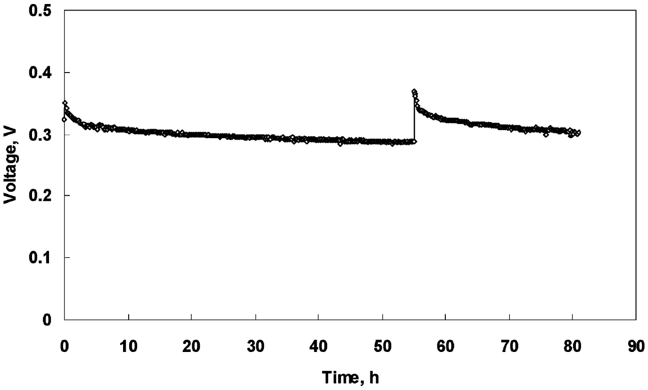

Figure 3. Durability test of catalyst Pt14−050 (1.4 nm, 0.5 mg/cm^2) at 100 mA/cm^2. The test was restarted after being run for 55 h and was then operated for another 25 h.

Nyquist diagrams of the anode and cathode were recorded in the beginning and after 55 h durability test (see the Supporting Information). A significant increase in impedance at the low frequency arc can be observed at the anode side, whereas only a slight increase was found at the cathode side. This suggests that the voltage loss during the durability test might be mainly due to the degradation of the catalysts on the anode side. The good stability of catalyst Pt14-050 might be attributed to the low loading of Pt metal on the cathode side, which reduces the liability of aggomeration.

In conclusion, a series of Pt nanoparticles were prepared with different sizes, ranging from 0.8 to 3.2 nm. The DMFC tests indicate that the samples with particle sizes less than 2 nm demonstrate better performances at the cathode side, and the noble metal loading can be markedly reduced. The premier durability test showed that the small-sized Pt nanoparticles are stable after the test was run for 55 h at 90 °C. Therefore, these small Pt nanoparticles show a great potential in DMFC applications.

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Supporting Information Available: Seed-growth catalyst preparation, TEM images of the supported catalysts, polarization curves, power densities plots, and impedance data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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