

Short communication

Nano-structured Pt–Cr anode catalyst over carbon support, for direct methanol fuel cell

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Abstract

In this study, several kinds of carbon were used as the support for the Pt-based catalyst of the direct methanol fuel cell (DMFC). Mesoporous carbons with large BET surface area and a commercial carbon were used as the support for the anode catalyst. The maximum current densities of the catalysts were compared by cyclic voltammogram. The catalyst supported on Vulcan XC-72, the commercial carbon support, showed the highest catalytic activity because of its high electric conductivity in spite of small BET surface area. Transition metals such as Cr, Mn, Y, or Zn were impregnated simultaneously with a Pt precursor on Vulcan XC-72, respectively, and then the catalytic activity was tested. The Pt–Cr/C catalyst showed the highest catalytic activity among this catalyst series, and was more active than the Pt/C catalyst. Furthermore, in order to improve the activity of the Pt–Cr/C catalyst, sintering of active metals by thermal reduction during the preparation should be avoided. Therefore, alkaline aluminum leaching method was applied for the purpose of decreasing the particle size of the active metals by reducing the sintering of Pt and Cr. Aluminum precursor was introduced together with Pt and Cr precursors into the commercial carbon support in the preparation process. After reduction of the sample, aluminum species were selectively leached out. The catalyst showed a much improved activity as expected and characterized by H₂ chemisorption and TEM analyses.

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1. Introduction

The Pt-based catalyst with a co-catalyst, Ru, which is supported on carbon is the general anode catalyst for direct methanol fuel cell (DMFC) [1]. Being different from other types of fuel cell, the DMFC needs no fuel processor to reform hydrocarbon fuels, making DMFC advantageous for application to the small and portable devices. One of the main problems in DMFC, though, is the inherently low power density. The insufficient activity of the anode catalyst is still an obstacle to overcome. In order to improve the catalyst perfor-

mance, many studies have been done on the electro-oxidation of methanol [2–6]. To date, the Pt-based alloys remain as the most active catalysts for the reaction [7]. Only a few electrocatalyst compositions have been proposed as alternatives to Pt for the electro-oxidation of methanol fuel. Because the substitutes employed in most studies have been noble metals such as osmium and iridium, the problem of high cost in DMFC remains unsolved. The most troublesome point is that the activity of the catalyst without noble metal is lower than that of the Pt-based electrocatalyst [8].

Since attempts to improve the activity of an anode catalyst without Pt group elements has not been highly successful, the development of the Pt-based binary catalyst supported on various carbons was employed in this paper. Ruthenium is

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known as a good co-catalyst for Pt in the electro-oxidation of methanol [9]. However, it attributes to the high manufacturing cost of the anode catalyst, thus making commercialization of the fuel cell more difficult. Therefore, in this study, Pt, a noble metal, was supported on several homemade porous carbons and carbon nanotubes as well as one commercial carbon. To improve the activity of the Pt/C catalyst, a transition metal was doped, and a new impregnation method of leaching-out was introduced for increasing the dispersion of the metal supported on carbon.

2. Experimental

2.1. Catalyst preparation

The 20 wt.% Pt/C catalysts for the anode of the DMFC were prepared by conventional impregnation method using various carbons, such as homemade mesoporous carbons (MC), carbon nanotubes (CNT), and a commercial carbon (Cabot, Vulcan XC-72). The mesoporous carbons were synthesized following a literature method [10]. Briefly, in an aqueous colloidal silica sol suspension of 40 wt.% silica in water (Aldrich, Ludox HS-40), resorcinol (Aldrich, ACS reagent) was polymerized with the aid of formaldehyde (37 wt.% aqueous solution, Junsei, ACS reagent). After the carbonization and subsequent HF etching of the composite, the final mesoporous carbon product was prepared. The carbonization was performed under nitrogen atmosphere by heating from room temperature to 850 °C at a rate of 5 °C/min. The composite was then held at 850 °C for 1 h. The etching was performed by stirring the resultant silica-carbon composite in an aqueous HF solution (48 wt.%, J. T. Baker, ACS reagent) for 12 h under ambient conditions. The carbon material was retrieved by filtration and washed repeatedly by deionized water. This mesoporous carbon was hereinafter labeled MC 1. When the carbonization temperature was increased from 850 to 1050 °C, the resulting carbon support was labeled MC 2. The carbon nanotubes were prepared by using CO/H₂ mixing gas according to the method reported by Chung [11] and labeled CNT 1 and 2.

H₂PtCl₆·6H₂O (Acros, ACS reagent) was used as a Pt precursor and supported on various carbon supports. In the case of the bimetallic catalyst; Cr(NO₃)₃·9H₂O (Hanawa, EP), MnHPO₄·3H₂O (Wako, EP), Zn(CH₃COO)₂·2H₂O (Hanawa, EP), and Y(NO₃)₃·6H₂O (Aldrich, 99.9%) were used as co-precursors. The co-precursors were added to the Pt precursor at a metal mole ratio of 1:1, respectively. The metal precursors were dissolved in deionized water (5.4×10^{-8} S cm⁻¹), and aqueous solution was impregnated on Vulcan XC-72 and then dried, milled, and thermally treated in a reducing atmosphere of 5 vol.% H₂/N₂.

To depress the sintering of the Pt-Cr/C catalyst during the activation process at high temperature, Al species were introduced into the catalyst system together with active metal components and removed selectively by alkaline alu-

minum leaching [12]. Al(NO₃)₃ (Junsei, EP) was used as an Al precursor, and was dissolved simultaneously with Pt and Cr precursors in the deionized water. The solution was then impregnated to the carbon support, followed by drying, milling, and reduction in the H₂/N₂ gas stream. After reduction of the catalyst precursor, only aluminum species of the Pt-Cr/C catalyst-containing aluminum species were selectively leached out by NaOH 20 wt.% aqueous solution, and finally the Pt-Cr/C catalyst was produced by the new method.

2.2. Catalytic activity test

The activity of the newly prepared catalysts was evaluated by checking the maximum current density of electro-oxidation of methanol in the half-cell test. The half-cell was a three-electrode cell system. As fuel, 1.0 M methanol was used. The catalyst was loaded with Nafion binder on a graphite rod (Gamry Instruments, 935-00003) as a working electrode. A Pt mesh electrode (Princeton Applied Research, 219810) and a saturated calomel electrode (Princeton Applied Research, K0077) were used as a counter electrode and a reference electrode, respectively. All the potential employed in this paper were recorded with respect to a normal hydrogen electrode (NHE). The activity test was performed in a 0.5 M H₂SO₄ aqueous solution after purging with nitrogen gas for the removal of dissolved oxygen in the water. Cyclic voltammogram was recorded with a potentiostat (Gamry Instruments, PC4/750) at the constant temperature of 40 °C in a water jacket type reactor.

2.3. Characterization

The BET surface area and pore size distribution were determined by N₂ adsorption and desorption using a porosimetry analyzer (Micromeritics Corp., ASAP 2010). Electric conductivity was checked using four-point probing equipment and a digital source meter (Keithley, 2400). For temperature-programmed reduction (TPR) analysis, TCD signal was detected by an A/D converter at the end of the flow through the catalyst-containing cell which was heated at a rate of 10 °C/min. The atomic elements in the leaching-out solution after filtration were analyzed using an ICP-atomic emission spectrometer (Shimadzu, ICPS-1000IV). The dispersion of metals was determined by volumetric H₂ chemisorption following a blank test of carbon support without active metals. The reduced catalysts were dried at 120 °C, then cooled down to room temperature and evacuated under a vacuum at a pressure of about 10⁻² Torr. The TEM (JEOL, JEM-2000EXII) was operated at 200 kV accelerating voltage using Cu α as radiating source. The material was dispersed in ethanol in an ultrasonic bath. Then, a drop of suspension was dispersed on a Cu grid. The TEM images were analyzed by statistical method using an image solution program (Media Cybernetics Inc., Image-Pro Plus).

Table 1
BET surface area and electric conductivity of various carbon supports

Carbon	BET surface area (m ² g ⁻¹)	Electric conductivity (S cm ⁻¹)
MC 1	1940	3.0×10^{-2}
MC 2	1320	4.0×10^{-1}
CNT 1	212	2.8×10^{-2}
CNT 2	510	1.7×10^{-1}
Vulcan XC-72	225	5.0

3. Results and discussion

3.1. Carbon support for an anode catalyst

Carbon has been so far confirmed to be the best support for DMFC catalyst. Due to its large surface area, high-loading amount of active metal is possible on carbon. In order to meet such a requirement, various carbon supports, e.g., several homemade carbons and a commercial carbon, were used in this work for preparation of the Pt/C catalyst. Table 1 shows the BET surface areas of these homemade mesoporous carbons. MC 1 had a large BET surface area of 1940 m² g⁻¹. However, the catalyst of Pt/C supported on MC 1 showed no electro-oxidation activity as indicated in Fig. 1 by a cyclic voltammetry experiment. This result was not acceptable when considering only the BET surface area. In order to clarify the reason why the catalyst had no methanol oxidation activity, the contact electric conductivity of carbon support was measured. The electric conductivity of MC 1 was much lower than that of Vulcan XC-72, suggesting that the low electric conductivity was responsible for the low activity of the catalyst supported on MC 1 (Table 1). In order to increase the electric conductivity of the mesoporous carbon, the car-

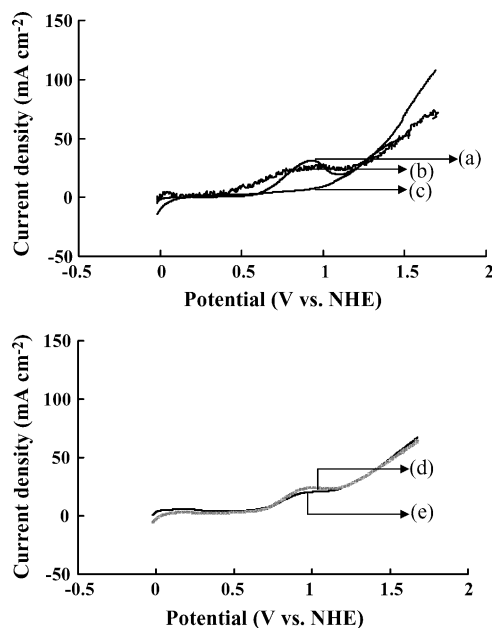


Fig. 1. Catalytic activities of Pt/C catalysts supported on several carbons: (a) Vulcan XC-72, (b) MC 2, (c) MC 1, (d) CNT 2, and (e) CNT 1.

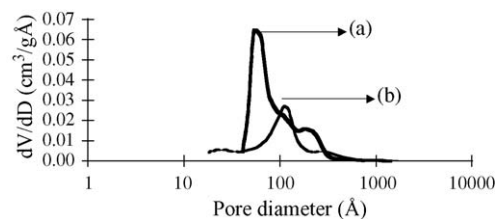


Fig. 2. Pore size distributions of homemade mesoporous carbons: (a) MC 1 and (b) MC 2.

bonization temperature was further increased. The thermal treatment of a carbon source at higher temperatures makes the carbon more electrically conductive because it gets more graphitized [13]. For comparison, several kinds of carbon nanotubes with good electric conductivity were used instead. As shown in Fig. 2, the MC 2 still showed meso-sized pores, of which the major pore size was 11 nm. However, the pore volume decreased due to pore collapse caused by high carbonization temperature. Table 1 shows the decrease of the BET surface area of MC 2 and the coinciding increase of electric conductivity. The activity of methanol electro-oxidation over the catalyst supported on MC 2 was shown in Fig. 1. Furthermore, several kinds of carbon nanotube series were also studied. The physical properties of each carbon are summarized in Table 1. As indicated in Fig. 1, all the Pt/CNT catalyst showed lower maximum current density than the Pt/Vulcan XC-72 for methanol oxidation. Regardless of surface area, Pt catalysts supported on CNT series were not highly active because their electric conductivities remained low, resulting in hard electron transfer from catalyst to the electrode.

Finally, the most active catalyst was the Pt on Vulcan XC-72 due to its high electric conductivity of 5 S cm⁻¹. This conductivity was 10–100 times higher than that of MC series and CNT series. Therefore, Vulcan XC-72 was used as support in this study for preparation of Pt-based binary catalysts.

3.2. Promotion effect of a transition metal on Pt/C

One mole of an electro-oxidation intermediate of methanol, (CO)–Pt, reacts with a water molecule adsorbed on a co-catalyst and generates two more moles of electrons [14]. This kind of reaction results in higher catalytic activity. So far, Ru has been known as the most successful co-catalyst because of its electronic and bifunctional effect. The electronic effect can be explained as the modification of the electronic environment around the Pt-sites [15]. The bifunctional effect means that the methanol residues such as CO adsorbed on Pt-sites react with the oxygenated species present on the neighboring Ru sites producing CO₂ [16]. In DMFC, however, Ru co-catalyst has not yet been commercially used because it is an expensive noble metal. In the efforts to increase the performance of the Pt/C catalyst, several transition metals were introduced instead of Ru as candidates for the binary Pt-based catalyst. In Fig. 3, the activities of binary Pt–M/C (M: Cr, Mn, Zn, and Y) catalysts are shown. The highest maximum current

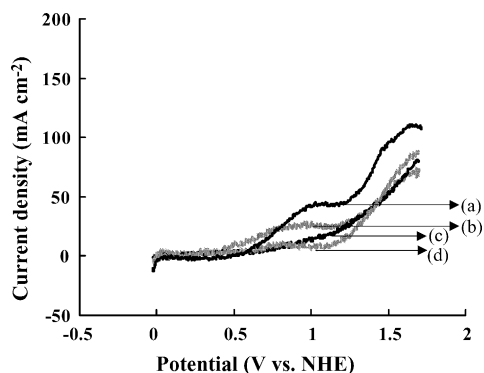


Fig. 3. Catalytic activities of Pt-M/C catalysts supported on Vulcan XC-72. M: (a) Cr, (b) Mn, (c) Zn, and (d) Y.

density was 48 mA cm^{-2} – higher than that of Pt/C catalyst – and was obtained when Cr was doped with Pt. Among the transition metals, Fe, Cr, and Ni, is known to adsorb H_2O molecules easily [17]. When Cr is doped with Pt, $(\text{CO})\text{-Pt}$, which is a partial oxidation product of methanol on platinum, reacts with $(\text{HOH})\text{-Cr}$, an adsorbed intermediate of H_2O on Cr [6]. This suggests that two more moles of electrons could be generated from one mole of methanol. That means higher maximum current density of the Pt–Cr/C catalyst than that of the Pt/C catalyst.

Furthermore, in order to enhance the activity of Pt–Cr/C catalyst, the reduction temperature of the catalyst precursor was optimized in the range of $300\text{--}600^\circ\text{C}$, because Cr species was not completely reduced to metal at 300°C . In Fig. 4, the activities of catalysts reduced at $300, 400, 500^\circ\text{C}$, and 600°C are shown. When the catalyst was reduced at 500°C , it had the highest activity. To investigate the different reduction temperature of Cr and Pt, temperature-programmed reduction (TPR) was performed for the Pt–Cr/C catalyst calcined in air at 600°C . The Pt/C catalyst was also analyzed after the calcination at the same temperature of 600°C (see Fig. 5). Both the Pt–Cr/C and the Pt/C catalysts had reduction peaks at 180 and 210°C ; these were also the Pt reduction peaks. The Pt–Cr/C catalyst, however, still showed peaks above 300°C . It is generally known that a noble metal such as Pt can be

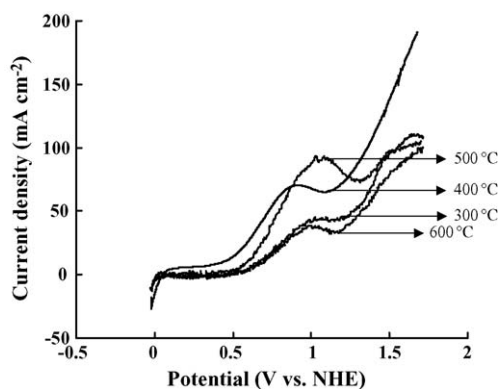


Fig. 4. Catalytic activities of Pt–Cr/C catalyst reduced at $300, 400, 500,$ and 600°C .

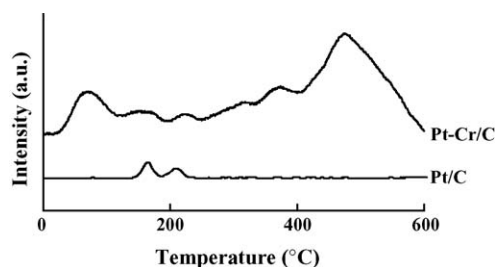


Fig. 5. TPR patterns of calcined Pt–Cr/C and Pt/C catalysts.

easily reduced at lower temperatures than transition metals. When the Pt–Cr/C catalyst was reduced at 300°C , there remained oxides of Cr in the catalyst, resulting in lower catalytic activity. When the TPR result is considered, as in the full reduction of Cr at 500°C , the maximum current density is shown at its highest level. Actually, the Pt–Cr/C catalyst showed the maximum current density of 90 mA cm^{-2} . The maximum current density of the Pt–Cr/C catalyst reduced at 600°C was decreased due to the sintering of active metals. It is consistent with the report by Lasch et al. which showed that over 600°C , the particle size of the platinum metal was significantly increased because of sintering [18]. Therefore, a volcano curve was obtained for methanol electro-oxidation activity versus reduction temperature.

3.3. Improvement of the Pt–Cr/C catalytic activity

Because Cr was added for enhancing the catalytic activity, the reduction temperature of the catalyst was increased, compared with the Pt/C catalyst. The reduction at high temperature means that a sintering phenomenon would severely occur to the catalyst, resulting in low dispersion of the active metal. In order to improve the dispersion of the Pt–Cr/C catalyst, depressing of the sintering of Pt and Cr during the reduction process is essential. Therefore, to decrease the sintering of the active metals, Al precursor was introduced together with Pt and Cr precursors on the carbon support at 20 mol% with respect to total metals in the preparation process. After reduction of the sample, the aluminum species were selectively leached out. Pt and Cr of the Pt–Cr/C catalyst were not dissolved in the final leaching-out solution, which was confirmed by testing ICP analysis; only aluminum species was detected in the leaching-out solution.

Cyclic voltammetry (CV) results of two different Pt–Cr/C binary catalysts are shown in Fig. 6. The Pt–Cr/C catalyst prepared by the new method showed enhanced activity at a maximum current density of 110 mA cm^{-2} . This was an increase of 20% as compared with the Pt–Cr/C catalyst prepared by the conventional impregnation method. It was thought that the sintering of metals was depressed by the newly proposed preparation method, because aluminum species between active metals hindered the sintering of those during the reduction at high temperature. The particle size of active metals was also reduced.

Table 2
Dispersions of Pt–Cr/C binary catalysts

Preparation method	Catalyst amount (mg)	Total metals (mmol)	H ₂ adsorbed (mmol)	H adsorbed (mmol)	Dispersion (%)
Conventional	51	0.17	0.007	0.014	8
Proposed	41	0.13	0.008	0.017	13

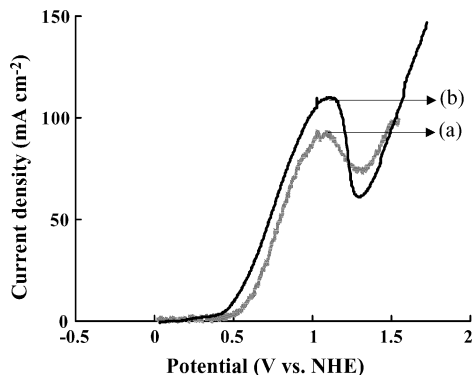


Fig. 6. Catalytic activities of Pt–Cr/C catalysts prepared by impregnation method: (a) conventional and (b) proposed.

To clarify the improved catalytic activity of Pt–Cr/C by the new catalyst preparation process, the catalysts were characterized by several methods. To compare the metals dispersion of the two binary Pt–Cr/C catalysts, H₂ was chemically adsorbed on the catalyst surfaces in a vacuum chamber, then the volume of adsorbed H₂ was detected. The results are shown in Table 2. At first, the total amounts of metals were calculated from the two different 40 wt.% Pt–Cr/C catalysts, 0.17 mmol and 0.13 mmol, respectively. Then, moles of hydrogen molecules adsorbed on the surfaces of the metals could also be evaluated from the extrapolation of H₂ moles

adsorbed when the pressure in the vacuum chamber was at zero. Therefore, the number of surface metals was determined using the assumption that one atom of metal chemisorbs one hydrogen atom because H₂ shows a dissociative chemisorption behavior on both Pt and Cr, respectively. The Pt–Cr/C catalyst by the conventional method showed 8% dispersion of metals, and the catalyst by the proposed method showed 13% dispersion. Thus, it was confirmed that dispersion of metals was increased because of decreased sintering phenomenon during the reduction by the new method of using alkaline aluminum leaching.

Finally, TEM analysis was performed. Two kinds of the Pt–Cr/C catalysts were prepared by the conventional impregnation and the new method in this study. If the added aluminum species was able to prevent the catalyst from sintering successfully, the smaller particles of metals would be detected. In Fig. 7, the TEM images of the two binary Pt–Cr/C catalysts are shown, respectively. When the catalyst was prepared by the newly proposed method, the dispersion of metals—including Pt and Cr—was increased and the metal particles are more homogeneous than those of another catalyst prepared by conventional method. Furthermore, in Fig. 8, statistical analysis of TEM images also showed that the distribution of metal particle size was narrow and the particle size was decreased in the case of the Pt–Cr/C catalyst prepared by the aluminum leaching-out method.

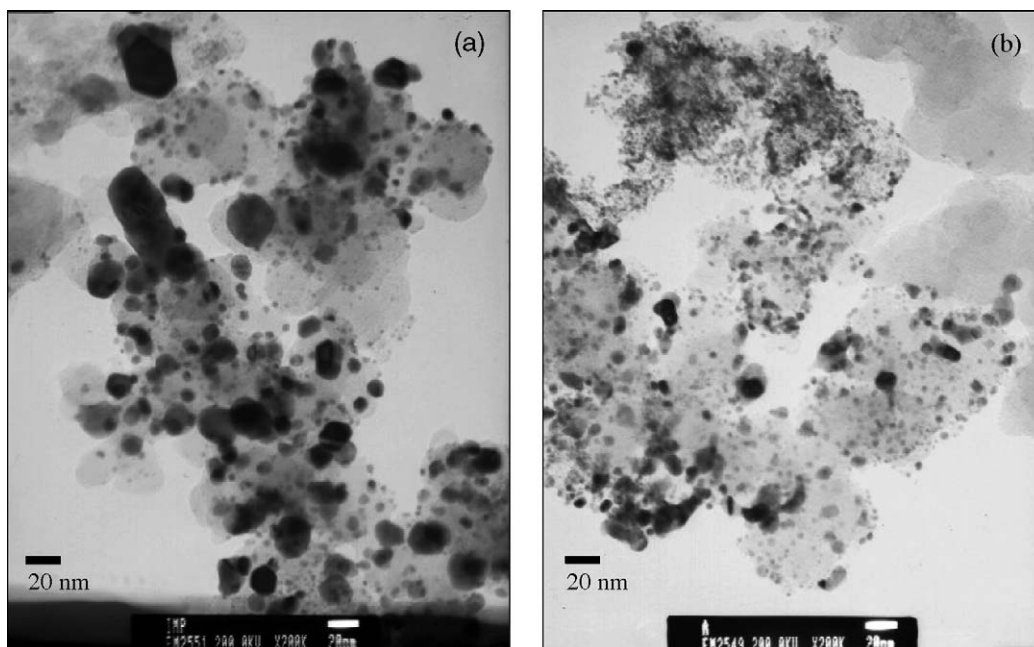


Fig. 7. TEM images of Pt–Cr/C catalysts prepared by impregnation method: (a) conventional and (b) proposed.

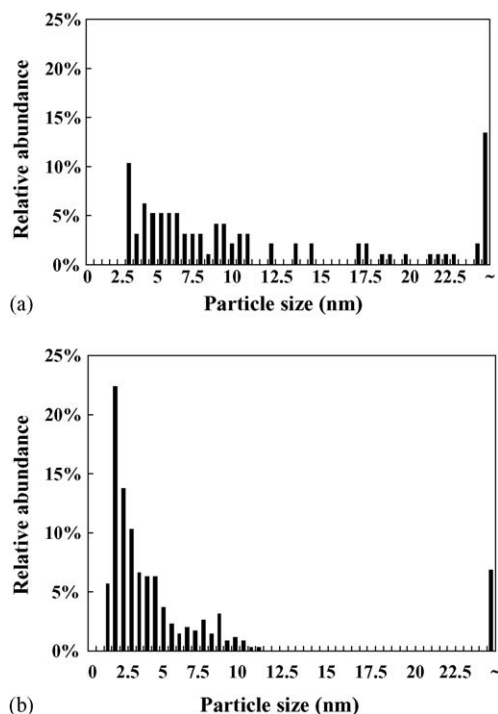


Fig. 8. The statistical analysis of metal particle size of Pt–Cr/C catalysts prepared by impregnation method: (a) conventional and (b) proposed.

4. Conclusions

From the results of the catalytic activity test of methanol electro-oxidation, Pt catalyst supported on Vulcan XC-72 showed the highest activity when compared with catalysts supported on homemade carbons and commercial one. This is due to its highest electric conductivity in spite of small BET surface area. To increase the activity of the Pt-based catalyst supported on Vulcan XC-72, Cr was doped with Pt on carbon support. The resultant Pt–Cr/C binary catalyst showed higher maximum current density than the Pt/C catalyst. Furthermore, the Pt–Cr/C binary catalyst demonstrated an enhanced catalytic activity when prepared by aluminum species insertion into the Pt–Cr/C catalyst and subsequent

selective leaching-out, resulting from higher and more homogeneous dispersion of active metals.

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