



Short communication

Support effect of anode catalysts using an organic metal complex for fuel cells

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ABSTRACT

The carbon support effect of Pt–Ni(mqph) electrocatalysts on the performance of CO tolerant anode catalysts for polymer electrolyte fuel cells (PEFCs) was investigated using carbon black and multi-walled carbon nanotubes (MWCNTs), with and without defect preparation. 20%Pt–Ni(mqph)/defect-free CNTs showed a very high CO tolerance (75% compared to the CO-free H₂ case) under 100 ppm CO level in the half-cell system of the hydrogen oxidation reaction. On the other hand, the hydrogen oxidation current on Pt–Ni(mqph)/defective CNTs, Pt–Ni(mqph)/VulcanXC-72R and Pt–Ru/VulcanXC-72R significantly decreased with increasing concentration of CO up to 100 ppm (25–47% compared to the CO-free H₂ case). It is thus considered that the carbon support materials strongly affect the CO tolerance of anode catalysts. This is ascribed to a change in the electronic structure of the Pt particles due to the interaction with the graphene surface, leading to a reduction in the adsorption energy of CO. Ni(mqph) also mitigates CO poisoning due to its ability of CO coordination on Ni metal center.

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1. Introduction

In recent years, fuel cells with high-energy efficiency have attracted much attention as environment-friendly energy conversion devices. Especially, polymer electrolyte fuel cells (PEFCs), for their low operating temperature (60–100 °C) capability and fast start up, are expected to be a suitable candidate in applications such as small-to-medium scale electric generators, transportation applications and portable power sources [1–3].

One of the most serious problems of stationary PEFCs for the commercialization is the poisoning of the anode catalyst by the CO present in the H₂ gas produced upon the reforming reactions of hydrocarbons [4,5]. Numerous catalytic studies have thus been reported concerning the CO tolerant anode. It has been known that Pt–Ru alloy catalysts (Pt–Ru/C) exhibit an electrochemical activity higher than that of pure Pt in the presence of 50–100 ppm CO [6,7]. However, the cell voltage obtained with the Pt–Ru/C anode in the presence of 100 ppm CO is still too far from being acceptable for practical applications. Moreover, there is still a barrier for the true commercialization of the metal alloy catalysts because of the cost and low natural abundance of the precious metals.

It has been reported that the performance of electrocatalysts in PEFC is enhanced by using carbon nanotubes (CNT) as a support material. Matsumoto et al. have reported that Pt supported on

carbon nanotubes (Pt/CNTs) can lead to the reduction of Pt usage by up to one third compared to that of Pt supported on a carbon black (Pt/CB) anode [8,9]. Yoo et al. have reported that Pt–Ru supported on CNTs (Pt–Ru/CNTs) revealed a very high CO tolerance in the hydrogen oxidation reaction (HOR) and methanol oxidation reaction (MOR) [10,11]. It is thought that CNTs have very good electrical conductivity and excellent durability compared with carbon black (CB) [12]. In these studies, thick multi-walled carbon nanotubes (MWCNTs) were used, as they are less expensive compared with single walled carbon nanotubes (SWCNTs). It can be regarded that the surface of MWCNTs is composed of graphene sheets because the curvature of the MWCNTs is small. The flat CNT surface is possibly effective for the formation of a triple-phase boundary (gas–electrode–electrolyte), which is important for the electrode reactions in a fuel cell, and the flat interface between CNTs and metal catalysts is expected to modify the catalytic properties of Pt–Ru particles.

It has also been reported that electrocatalysts using organic metal complexes show good performance in PEFC. Okada et al. have reported that Pt–VO(salen)/VulcanXC-72R and Pt–Ni(mqph)/VulcanXC-72R revealed very high CO tolerances when compared with Pt/C and Pt–Ru/C alloy catalysts [13–17]. Here abbreviated ligand names are salen: *N,N'*-bis(salicylidene)ethylenediamine and mqph: *N,N'*-mono-8-quinolyl-*o*-phenylenediamine, which are featured as central metal-N coordination structures and peripheral aromatic rings [16,17]. The chemical structure of Ni(mqph) is shown in Fig. 1. It is considered that anode catalysts consisting of Pt and organic metal

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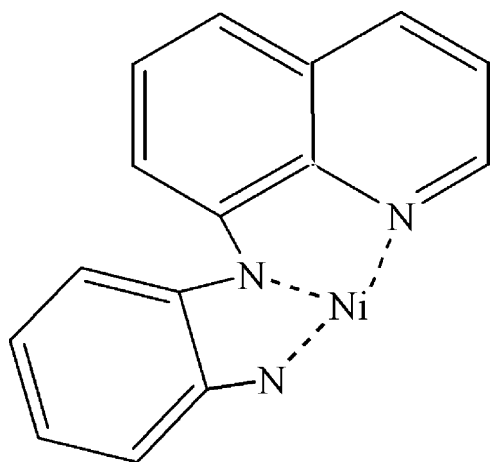


Fig. 1. Chemical structure of Ni(mqph): *N,N'*-mono-8-quinoyl-*o*-phenylene-diamine-nickel.

complexes are expected to be good candidates as the CO-tolerant anode catalysts of PEFCs. Pt metal particles surrounded by organic metal complexes are formed on the carbon substrate after the heat treatment in an inert gas. These metal complexes are partially decomposed from the peripheral, but the central metal-nitrogen coordination structures were assumed to exist intact [14,17].

Since the catalytic activity of Pt is enhanced by organic metal complexes, it is expected that the surface of the carbon support would further modify the catalytic function, and improve its CO tolerance. In this paper, Pt–Ni(mqph) electrocatalysts supported on CNTs and CB (VulcanXC-72R) are prepared and their CO tolerance in the hydrogen oxidation reaction (HOR) is compared by rotating disk electrode (RDE) experiments and half-cell experiments using a membrane electrode assembly (MEA) in a half-cell system.

2. Experimental

Carbon black (VulcanXC-72R) and multi-walled carbon nanotubes (abbreviated as CNTs; Shenzhen Nanotech Co. Ltd.) of 20–50 layers were used as the catalyst support. In the preparation of the CNTs, air oxidation pre-treatment was performed to investigate the influence of the surface state of CNT samples. The CNTs were purified by ultrasonic treatment for 1 h, refluxed in HNO₃ (14M) at RT for 2 h, poured into distilled water, and dried at 100 °C in air. The

CNTs obtained by these procedures are called defect-free CNTs in this study. Next, to generate the defects and to open the end of CNTs, the defect-free CNTs were oxidized in a quartz tube reactor by flowing air at 600 °C. Hereafter, the oxidized CNTs are called defective CNTs. Fig. 2 shows TEM images of the defect-free and defective CNTs. Many defects are observed for the defective CNTs as shown in Fig. 2b.

The organic metal complex, Ni(mqph), was synthesized as reported previously [15]. Composite catalysts including 20 wt.% Pt were prepared from the mixture of platinum precursor, i.e., platinum tetraamine chloride Pt(NH₃)₄–Cl₂·xH₂O, the organic metal complex Ni(mqph) and the carbon supports (VulcanXC-72R, defect-free CNTs and defective CNTs) in 3:3:4 mass ratios. The atomic ratio of Pt/Ni in the composite catalyst was estimated to be 1.2:1. The powders were dispersed in ethanol, dried in air at 40 °C for 60 min and then heat-treated under an Ar stream at 400 °C for 2 h in a furnace. After the heat treatment, the CO tolerance of the catalyst samples was examined by comparing the HOR current at various CO concentrations using RDE and the half-cell system.

The RDE test was performed in 0.1 mol dm^{−3} HClO₄ at 25 °C while bubbling pure hydrogen or a mixture of 1% CO and 99% H₂ through the system. Catalysts were loaded onto a glassy carbon disk electrode with a Pt content of 2.5 × 10^{−2} mg(Pt) cm^{−2} (apparent area) with diluted (1:50) 5% Nafion solution (Aldrich). Polarization curves were recorded at the scan rate of 5 mV s^{−1}, and the current at 0.1 V vs. RHE was sampled for evaluation of the HOR current under pure H₂ and 1% CO with H₂. A commercial 20%Pt–10%Ru/VulcanXC-72R (ElectroChem. Inc.) was also tested to compare the CO tolerance of the Pt–Ni(mqph) catalysts in the electrochemical measurements.

The half-cell equipment consists of a half-side membrane electrode assembly (half-MEA) with a Nafion[®] 115 membrane, and an Au mesh electrical contact in a Teflon holder with a gas inlet and outlet. The catalyst supported carbon powder (30 mg) abbreviated as Pt–Ni(mqph)/C, was mixed with 500 mg of 5 wt.% Nafion solution (Aldrich) together with 30 mg of ethanol and stirred, to get an ink of the mixture. This mixture was then transferred to the carbon paper disk (TORAY TGP-H-090, 0.3 mm in thickness, 8 mm in diameter) that was pretreated to a wet-proof condition with poly(tetrafluoroethylene) (PTFE, 3.3 × 10^{−3} g cm^{−2}). The amount of Pt in the mixed catalyst was 5.4 × 10^{−4} g(Pt) cm^{−2}, for the apparent electrode area of the disk. The half-MEA was prepared by hot-pressing the catalyst-loaded carbon paper disk to one side of the Nafion[®] 115 membrane at a pressure of 100 kg cm^{−2} at 130 °C for 3 min. H₂ gas containing 0, 10, 50, and 100 ppm CO was supplied to

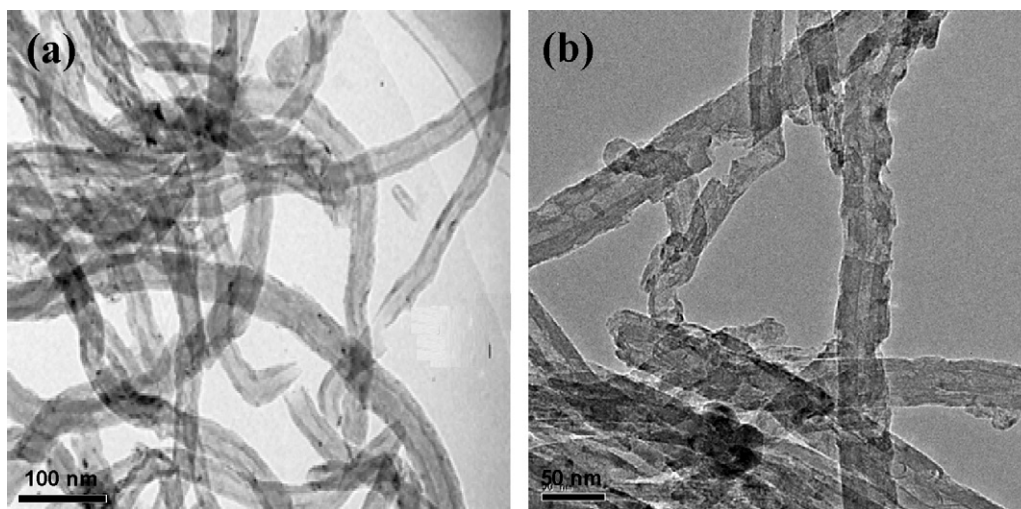


Fig. 2. TEM images of CNTs. (a) Defect-free CNTs and (b) defective CNTs.

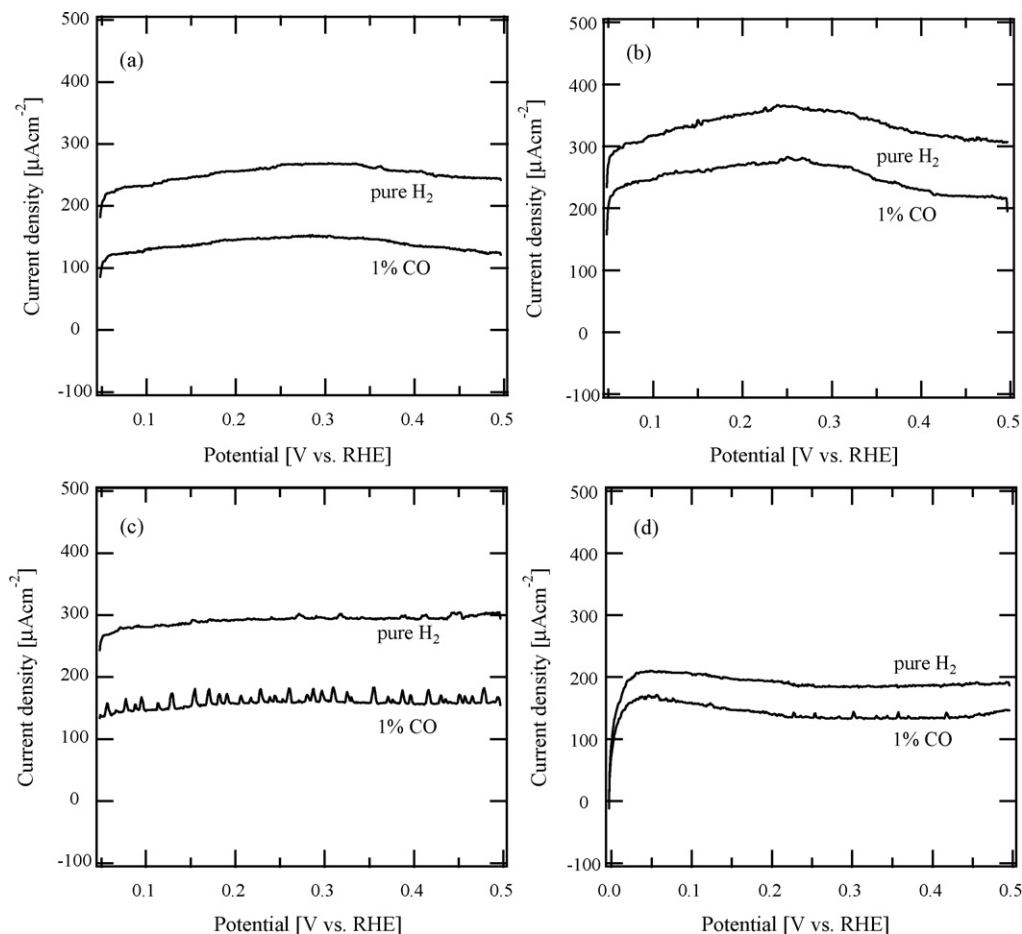


Fig. 3. RDE test with the 20%Pt–Ni(mqph)/C and 20%Pt–10%Ru/VulcanXC-72R. Polarization curves of hydrogen oxidation reaction on RDE measured in $1 \text{ mol dm}^{-3} \text{ HClO}_4$ at 25°C , where H_2 gas is bubbled without and with 1% CO. Rotation speed 300 rpm, potential scan rate 5 mV s^{-1} . (a) 20%Pt–Ni(mqph)/defective CNTs, (b) 20%Pt–Ni(mqph)/defect-free CNTs, (c) 20%Pt–Ni(mqph)/VulcanXC-72R and (d) 20%Pt–10%Ru/VulcanXC-72R.

the carbon paper side of the catalyst layer, and the Nafion[®] membrane side was in contact with $1 \text{ mol dm}^{-3} \text{ HClO}_4$ deaerated with N_2 gas and thermostated at 70°C . The flow rate of H_2 gas was $20 \text{ cm}^3 \text{ min}^{-1}$. The working electrode was the half-MEA with the catalyst-supported carbon paper disk that was in electrical contact with the Au mesh and Pt wire lead; the platinum plate and the reversible hydrogen electrode (RHE) in $1 \text{ mol dm}^{-3} \text{ HClO}_4$ were used as the counter and reference electrodes, respectively. After a steady rest potential was attained (about 1 h), the potential was scanned at a scan rate of 5 mV s^{-1} for the polarization measurement, in a potential range from 0 to 0.5 V vs. RHE, using a Solartron model SI 1287 potentiostat.

3. Results and discussion

Fig. 3 shows the results of the RDE test with the 20%Pt–Ni(mqph) catalysts supported on defect-free CNTs, defective CNTs and VulcanXC-72R in $0.1 \text{ mol dm}^{-3} \text{ HClO}_4$. The polarization curves of the HOR current were measured in pure H_2 and in 1% CO with H_2 . A rough CO tolerance tendency was obtained by comparing the HOR currents at 0.1 V vs. RHE both with and without CO. The HOR current density shown in Fig. 3 decreased in the presence of 1% CO by 56%, 78%, and 52% for Pt–Ni(mqph) catalysts on defective CNTs, defect-free CNTs, and VulcanXC-72R, respectively. That is, the electrocatalyst using defect-free CNTs shows the highest current, which was comparable to that measured for a commercial

20%Pt–10%Ru/VulcanXC-72R, 77% as a reference catalyst used with the same Pt amount.

In order to investigate in more detail the support effect obtained by the RDE results, polarization curve measurements and CO stripping experiments were performed with the half-cell system. The CO tolerance tests for the anode catalysts were carried out in the half-cell system at 70°C , consisting of the half-MEA with the Nafion[®] 115 membrane at the same Pt amount. Fig. 4 shows the current–potential curves of hydrogen oxidation for Pt–Ni(mqph)/defect-free CNTs, Pt–Ni(mqph)/defective CNTs, Pt–Ni(mqph)/VulcanXC-72R, and Pt–Ru/VulcanXC-72R in H_2 with various concentrations of CO. The preparation of the catalysts and subsequent current measurements were repeated to confirm the reproducibility of the data. In pure H_2 , the catalytic activities of all the electrocatalysts were not much different as shown in Fig. 4. In the presence of CO, however, the catalytic activity deviates depending on the support materials. For example, the catalytic activity of Pt–Ni(mqph)/defect-free CNTs is maintained above 80% under 100 ppm level CO as compared with the pure H_2 case. In contrast, the catalytic activity of Pt–Ni(mqph)/defective CNTs, Pt–Ni(mqph)/VulcanXC-72R and Pt–Ru/VulcanXC-72R decreased significantly with increasing CO concentration. Table 1 summarizes the hydrogen oxidation currents in the half-cell at 0.1 V vs. RHE measured for Pt–Ni(mqph)/C and Pt–Ru/VulcanXC-72R with the same Pt amount. The mass activities in pure H_2 were 4.23, 2.72, 4.48 and $3.44 \text{ A mg(Pt)}^{-1}$ for Pt–Ni(mqph) catalysts

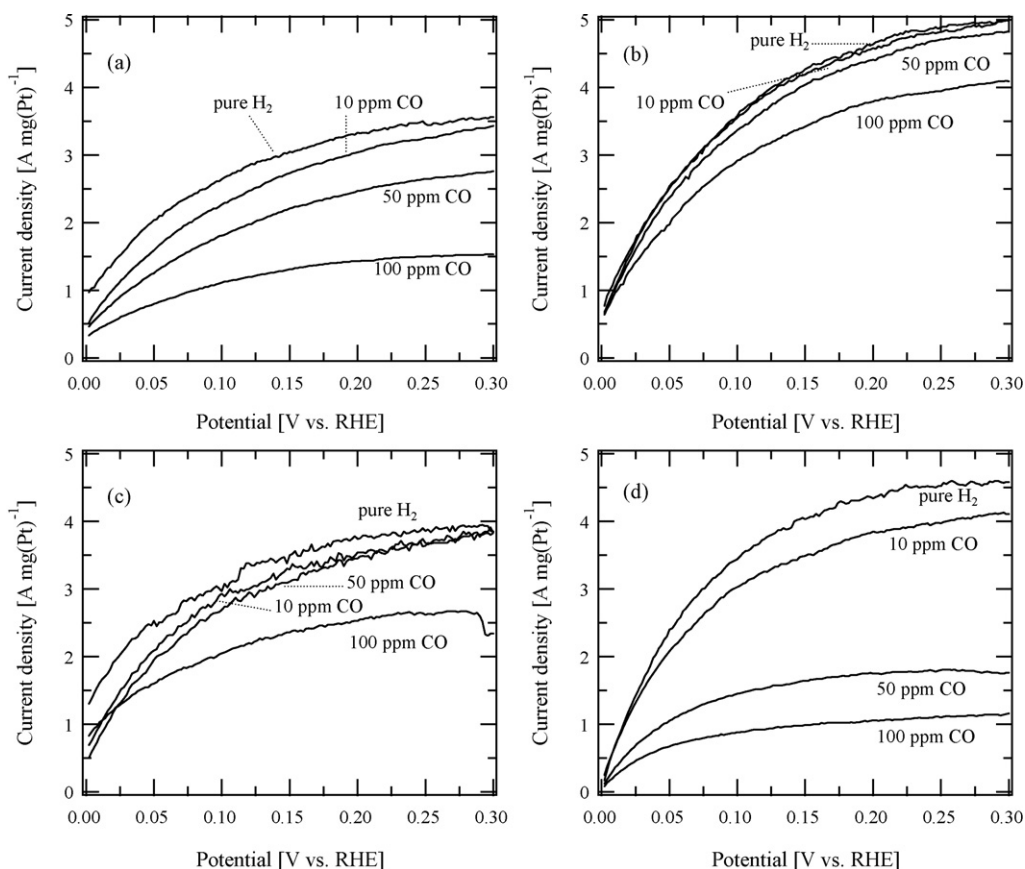


Fig. 4. Current–potential curves of hydrogen oxidation for 20%Pt–Ni(mqph)/C and 20%Pt–10%Ru/VulcanXC-72R measured in a half-cell system at 70 °C with H₂ gas containing various amounts of CO. (a) 20%Pt–Ni(mqph)/defective CNTs, (b) 20%Pt–Ni(mqph)/defect-free CNTs, (c) 20%Pt–Ni(mqph)/VulcanXC-72R and (d) 20%Pt–10%Ru/VulcanXC-72R.

supported on defect-free CNTs, defective CNTs, and VulcanXC-72R and Pt–Ru/VulcanXC-72R, respectively. The percentage of the currents in 10 and 100 ppm CO compared to the current in pure H₂ were 89% and 75% for Pt–Ni(mqph)/defect-free CNTs, 82% and 30% for Pt–Ni(mqph)/defective CNTs, 87% and 47% for Pt–Ni(mqph)/VulcanXC-72R, and 88% and 25% for Pt–Ru/VulcanXC-72R, respectively. The results indicate that the performances of the Ni(mqph) complex catalysts are high enough to sustain efficient H₂ oxidation in the presence of CO. Saito et al. have reported that the Pt–Ni(mqph)/VulcanXC-72R revealed high CO tolerance compared with Pt–Ru/C alloy catalysts, because Ni(mqph) will assist the CO tolerance by drawing CO from a Pt site to a Ni site that is surrounded by three N, and has open LUMO orbitals facing outward [16]. In the present study, better CO tolerances of the Pt–Ni(mqph) catalyst were obtained by using the defect-free CNTs as a support. It is thus found that the CO tolerance of anode electrocatalysts is dependent on the carbon support materials. This is ascribed to the different surface state of the carbon support. The flat surface structure of the CNTs consisting of graphene sheets may influence the morphology

or the electronic structure of Pt nanoparticles, which is currently studied by surface science approaches using a Pt-deposited HOPG (Highly oriented pyrolytic graphite) model catalyst in our group.

Fig. 5 shows the typical TEM images and the histograms of the particle size for Pt–Ni(mqph) catalysts supported on various carbon supports. The particle size distributions were obtained by directly measuring the size of 100 particles in the magnified TEM images. The average diameters were 2.4, 2.7, and 4.5 nm for Pt–Ni(mqph)/defective CNTs, Pt–Ni(mqph)/defect-free CNTs, and Pt–Ni(mqph)/VulcanXC-72R, respectively. The distribution of Pt particle sizes for the CNT supports is shown to be relatively narrow compared with that for the VulcanXC-72R support. It should be noted that no significant differences to explain the support effect were found between CNTs supports with and without defects in the TEM observation. That is, it is possible that the interface interaction between Pt–Ni(mqph) catalyst and the surface of CNTs influences catalytic activity greatly. Here, it is difficult to identify Ni(mqph) species in the TEM images because they probably exist as the invisible clusters of organic metal complex molecules [17].

Table 1

Comparison of H₂ oxidation currents at 0.1 V RHE on 20%Pt–Ni(mqph)/C and 20%Pt–10%Ru/VulcanXC-72R measured in a half-cell at 70 °C with H₂ anode gas containing various amounts of CO

Catalysts	Mass activity (A mg(Pt ⁻¹))/current ratio (%)			
	Pure H ₂	10 ppmCO/H ₂	50 ppmCO/H ₂	100 ppmCO/H ₂
20 wt.%Pt–Ni(mqph)/defect-free CNTs	4.23 (100)	3.76 (89)	3.54 (84)	3.17 (75)
20 wt.%Pt–Ni(mqph)/defective CNTs	2.72 (100)	2.23 (82)	1.36 (50)	0.82 (30)
20 wt.%Pt–Ni(mqph)/VulcanXC-72R	4.48 (100)	3.92 (87)	3.20 (71)	2.12 (47)
20 wt.%Pt–10 wt.%Ru/VulcanXC-72R	3.44 (100)	3.03 (88)	1.45 (42)	0.88 (25)

Current ratio was derived from the polarization curves normalized by hydrogen oxidation currents at 0.1 V vs. RHE in pure H₂.

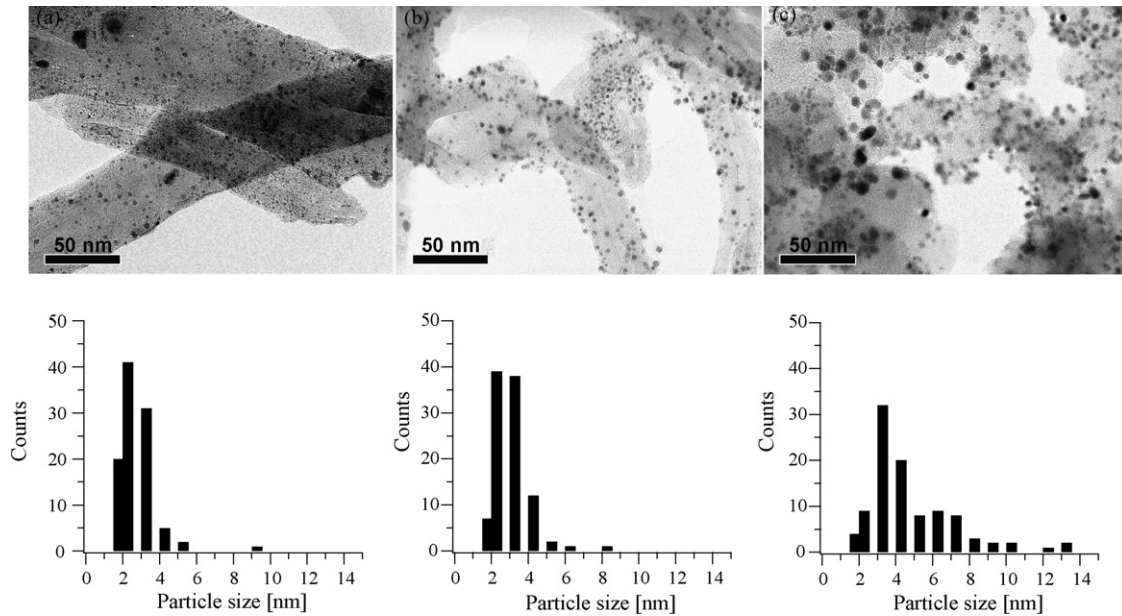


Fig. 5. The TEM image of 20%Pt-Ni(mqph)/carbon and histogram of the particle size estimated from 100 particles for Pt-Ni(mqph) catalysts supported on (a) defective CNTs, (b) defect-free CNTs, and (c) VulcanXC-72R.

Fig. 6 shows the CO_{ad} oxidation peaks observed during the anodic potential sweep of stripping tests using the half-cell system. The CO stripping test was performed after the linear sweep voltammetry experiment for CO tolerance, by switching the anode gas from 100 ppm CO/H_2 to N_2 . The CO_{ad} oxidation peaks of the Pt-Ni(mqph) catalysts were observed at around 0.7–0.8 V vs. RHE, for VulcanXC-72R and defective CNTs, respectively. In contrast, the CO_{ad} oxidation peak of the Pt-Ni(mqph)/defect-free CNT catalyst was not observed using linear sweep voltammetry for 100 ppm CO level. It is thus considered that the amount of CO adsorption

on the Pt-Ni(mqph)/defect-free CNTs is much lower compared to the other two samples. It is clear that the CO tolerance of the Pt-Ni(mqph) catalysts varied significantly on the carbon support material employed. The possible reason for the support effect of CNTs for PEFC is raised based on the different reactivity of flat graphene surfaces from that of the edged layers or amorphous carbon structures. Furthermore, the interaction between Pt-Ni(mqph) and graphene of CNTs may cause different electronic structures of Pt catalyst particles, mitigating the interaction of CO with Pt. It is possible that the d electron deficiency of Pt decreases

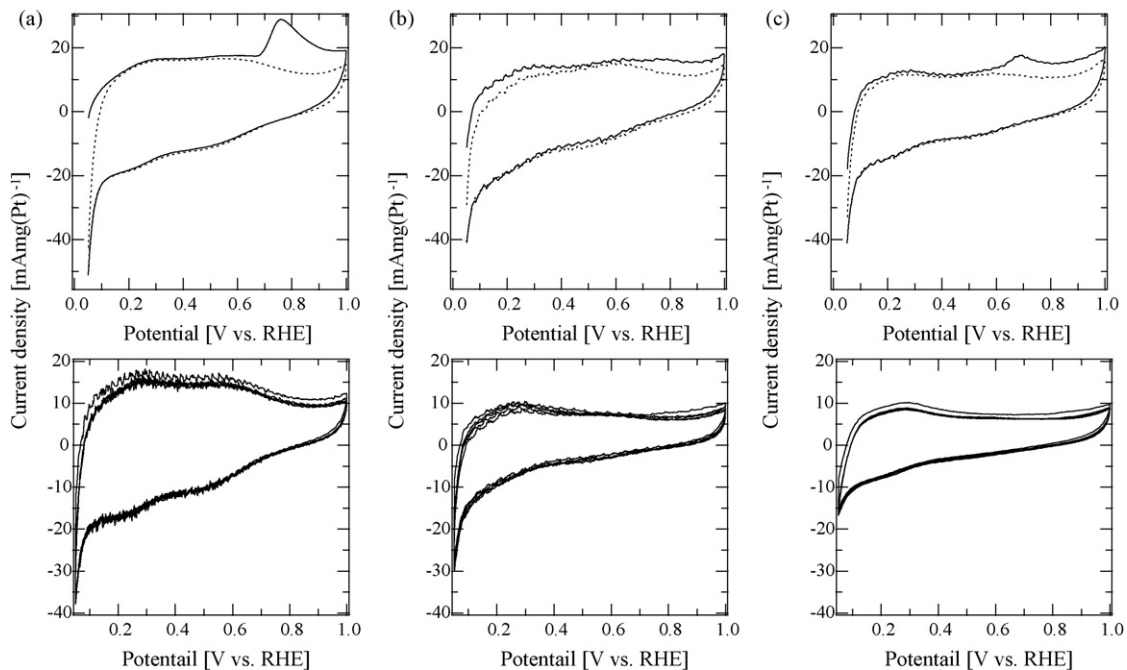


Fig. 6. CO stripping voltammetry after keeping the potential at 0.05 V RHE for 1 h measured in a half-cell system at 70 °C with H_2 gas containing 100 ppm CO. The solid line indicates the first, the dotted line indicates the second sweep. (a) 20%Pt-Ni(mqph)/defective CNTs, (b) 20%Pt-Ni(mqph)/defect-free CNTs, (c) 20%Pt-Ni(mqph)/VulcanXC-72R. For comparison, cyclic voltammograms measured in N_2 gas are shown in the bottom figures.

the back donation to the 2π orbital of CO and weakens the Pt–CO bond [18].

4. Conclusion

The carbon support effect of Pt–Ni(mqph) anode catalysts on the performance of CO tolerance in PEFCs was examined by electrochemical hydrogen oxidation reaction (HOR) measurements and CO stripping voltammograms. The HOR measurements showed that the 20%Pt–Ni(mqph)/defect-free CNTs electrocatalysts revealed the highest catalytic activity among Pt–Ni(mqph) catalysts supported on various carbon substrates. The current ratio of 20%Pt–Ni(mqph)/defect-free CNTs for 100 ppm CO/H₂ compared to pure H₂ was 75% in the half-cell test. The high catalytic activity of 20%Pt–Ni(mqph)/defect-free CNTs under a 100 ppm CO level was well reproduced. The CO stripping voltammogram also revealed that the CO_{ad} oxidation peak varied depending on the surface state of carbon support, where that of 20%Pt–Ni(mqph)/defect-free CNTs was not observed. The results of this work suggest that CNTs without surface defects are expected to be a good support material for the anode catalysts of PEFCs.

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