



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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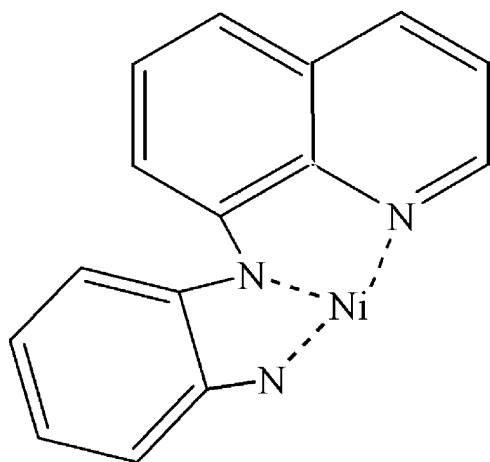


Fig. 1. Chemical structure of Ni(mqph): *N,N'*-mono-8-quinoyl-*o*-phenylenediamine-nickel.

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

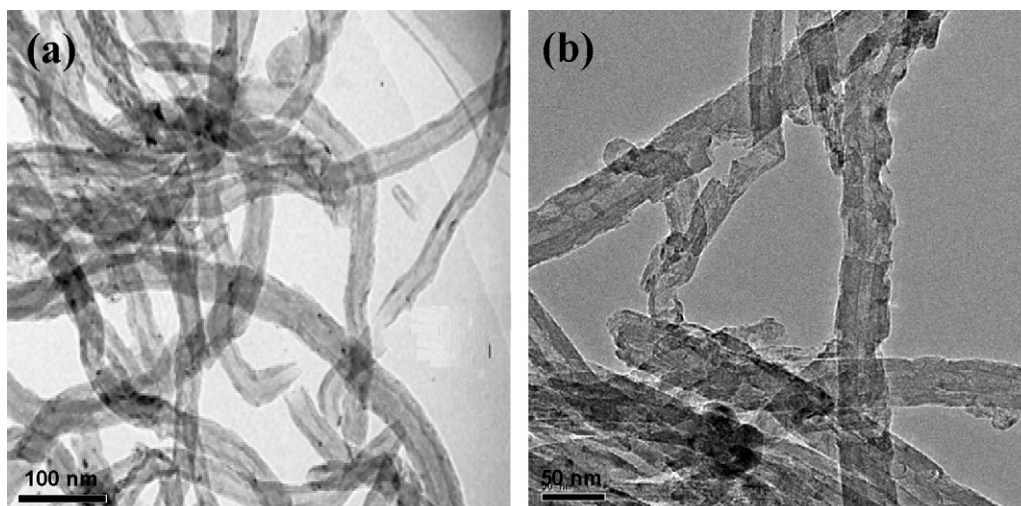


Fig. 2. TEM images of CNTs. (a) Defect-free CNTs and (b) defective CNTs.

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