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Preparation and Characterization of Palladium Nanoparticles Supported on Nickel Hexacyanoferrate for Fuel Cell Application

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Nickel hexacyanoferrate supported palladium nanoparticles (Pd-NiHCF NPs) were synthesized and studied for oxygen reduction reactions in direct methanol fuel cell. The NiHCF support was readily synthesized by a co-mixing of $Ni(OCOCH_3)_2$ and equimolar $K_3[Fe(CN)_6]$ solution into DI water under rigorous stirring. After the preparation of NiHCF support, Pd NPs were loaded on NiHCF *via* L-ascorbic acid reduction method at 80 °C. Pd-NiHCF NPs were electrochemically active for oxygen reduction reaction in 0.1 M $HClO_4$ solution. X-ray absorption near edge structure analysis was conducted to measure the white line intensity of Pd-NiHCF to verify the OH adsorption. As a comparison, carbon supported Pd NPs exhibited same white line intensity. This study provides a general synthetic approach to easily load Pd NPs on porous coordination polymers such as NiHCF and can provide further light to load Pd based alloy NPs on NiHCF framework.

Key Words : Direct methanol fuel cell, Oxygen reduction reaction, Palladium, Prussian blue, Hexacyanoferrate

Introduction

Palladium (Pd) nanoparticles (NPs) catalysts have attracted a great deal of attention due to their promising applications, particularly as the electrode catalyst for low-temperature fuel cells.[1-3] Although supported Pd NPs catalysts have excellent electrocatalytic activity in oxygen reduction reactions (ORR), they suffer from high temperature and complicated fabrication processes.[4-7] Therefore, it is of primary importance to fabricate low-cost and readily synthesized support materials for precious metals in fuel cells renewable energy field. Accordingly, recent researches and commercial developments of fuel cells have predominant aims at introducing new class of electrodes fabricated by cost-effective and environmentally-friendly processes.[8] Among the various nanostructured materials, nano-sized metal-organic frameworks (MOFs) have attracted growing interest owing to their unique properties and potential applications in various fields such as catalyst support, gas storage, and purification.[9,10] MOFs can be considered as the practicable candidates for new class of supports for precious metals because they possess tunable pores, high surface area and well defined structures.[11] Porous coordination polymers such as Prussian blue analogues, mixed-valence metal hexacyanoferrates (MHCFs), are representative materials for these open framework structures. They are generally prepared by simple synthetic procedures, and their physical properties are well studied.[12-14]

The rigid framework of MHCFs provides great durability for noble metal catalyst in corrosive and drastic reaction conditions including acidic and oxidative solutions. In addition, MHCFs prepared rapidly by an environmentally-friendly process and low cost precursors have attracted increasing attention as alternative supports to activate carbon for noble metal NPs.[15] MHCFs are solid-state compounds with face-centered cubic structure and idealized formula of $K_xM^{II}_y[Fe^{III}(CN)_6]$.[16-18]

In this study, we synthesized nickel hexacyanoferrate nanoparticles (NiHCF NPs) by using a simple and economical coprecipitation method. Pd NPs were loaded on NiHCF NPs support by a facile procedure and the activity of synthesized catalyst was evaluated for ORR applications in 0.1 M $HClO_4$ solution.

Experimental

Synthesis of Nickel Hexacyanoferrate Nanoparticles. In a typical synthesis, NiHCF NPs were prepared by slow and simultaneous addition of 100 mL of 0.01 M $Ni(OCOCH_3)_2$ and equimolar $K_3[Fe(CN)_6]$ solution into 100 mL of DI water under rigorous stirring at 50 °C. The solution was allowed to cool down to room temperature. The solid product was isolated by centrifugation, washed several times with water, and dried in vacuum at 90 °C.

Preparation and Characterization of Electrocatalysts. Pd (18.7 wt %) loaded on NiHCF NPs were prepared *via* L-ascorbic acid reduction method. Reducing metal precursor to metal nanoparticles with L-ascorbic acid has previously been reported in detail and took an advantage of that. Pd-NiHCF NPs were synthesized by using ethanol as a solvent and L-ascorbic acid as a reducing agent. 0.2 g of NiHCF NPs and 0.4 g of L-ascorbic acid, as a reducing agent, were dispersed in ethanol (200 mL) and stirred for 1 h and sonicated for 30 min. In sequence, certain amounts of Palladium(II) nitrate hydrate precursors were added to the mixture solution and kept in stirring condition for 1 h. After sonication for 3 min, the solution was heated to 80 °C in a three neck flask under an Ar atmosphere and maintained at the temperature for 3 h. After cooling to room temperature, the solution was filtered, washed with ethanol, and dried in a vaccum desiccator. The nanostructure materials were characterized by X-ray diffraction (XRD, Rigaku D/MAX 2500) operated with a Cu Kα radiation (40 kV, 100 mA). The size and morphology of the Pd-NiHCF NPs were confirmed by transmission electron microscopy (JEM 2100F, JEOL). X-ray photoelectron spectroscopy was performed to collect core level spectra of Pd (3d) using Al Kα source (Sigma probe, VG Scientifics).

K-edge valence band of Pd was obtained from the X-ray absorption near-edge spectroscopy (XANES), at the Pohang Accelerator Laboratory (PAL). XANES data were analyzed using ATHENA and ARITEMIS software of IFEFFIT programs.

Electrochemical Measurements. The catalyst ink slurry was prepared by mixing 0.01 g of Pd-NiHCF NPs with 20 μL DI water, 60 μL 5 wt % Nafion solution (Aldrich Chem. Co) as a binding material, and 700 μL isopropyl alcohol (IPA). After mixing and ultrasonicating, 7 μL of ink slurry was pipetted and dropped onto a glassy carbon substrate (geometric surface area 0.196 cm^2). Electrochemical measurements were carried out in an Autolab potentiostat (PGSTAT101) using a conventional three-electrode electrochemical cell comprised of a glassy carbon working electrode, a platinum wire counter electrode, and a saturated calomel reference electrode (SCE). All electrochemical measurements are quoted with respect to normal hydrogen electrode (NHE) and were conducted at 293 K. ORR polarization curves were obtained using a RDE 1,600 rpm, with scanning from −0.094 to 0.756 V *vs* SCE at 5 mV/s in 0.1 M $HClO_4$ under an O_2 flow.

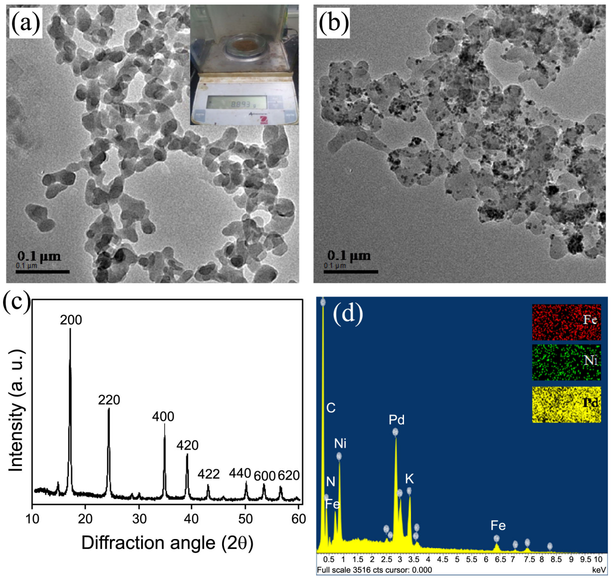

Figure 1. (a) TEM image of NiHCF NPs. The inset shows the photograph of NiHCF NPs synthesized in large-scale. (b) X-ray diffraction patterns of NiHCF NPs. (c) TEM image of -NiHCF NPs. (d) EDX profile of Pd-NiHCF NPs.

Results and Discussion

Characterization of Pd-NiHCF NPs Electrocatalysts. The transmission electron microscopy (TEM) images of NiHCF NPs and Pd-NiHCF NPs, shown in Figure 1(a), and 1(b) reveal that the NiHCF NPs have average diameters of *ca.* 20-50 nm and the Pd NPs with diameter of 2 nm are loaded on NiHCF NPs. NiHCF NPs can be readily synthesized in large scale using inexpensive precursors by a simple and fast process. For example, when 0.032 M of the starting materials were reacted in 1 L of deionized water, ~9 g of the NiHCF NPs could be obtained (Fig. 1(a) inset). X-ray powder diffraction patterns of NiHCF NPs showed diffraction peaks with indices 111, 200, 220, 400, 420, 422, 440, 600, and 620 for face-centered cubic structure of Prussian blue analogues (Figure 1(c)). The elemental analysis results using inductively coupled plasma mass spectroscopy, and CHN analysis also confirmed the formation of NiHCF and Pd-NiHCF. The energy dispersive X-ray spectrum (EDX) of the Pd-NiHCF catalyst shows that the Pd species are successfully immobilized on the NiHCF (Figure 1(d)). The existence of Pd NPs was confirmed by X-ray photoelectron spectroscopy (XPS)

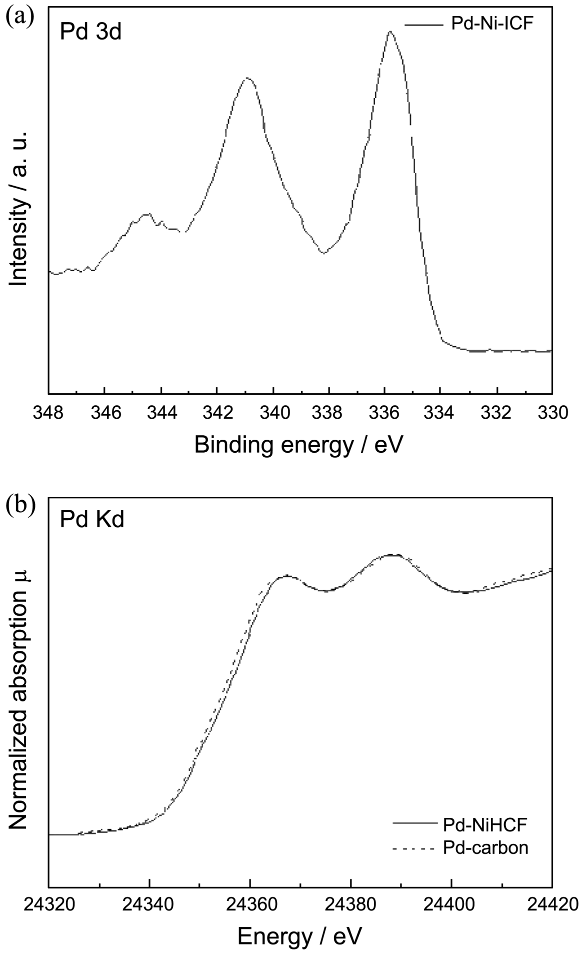

Figure 2. (a) The XPS spectra of Pd-NiHCF NPs. (b) XANES spectra of Pd-NiHCF NPs and Pd-carbon.

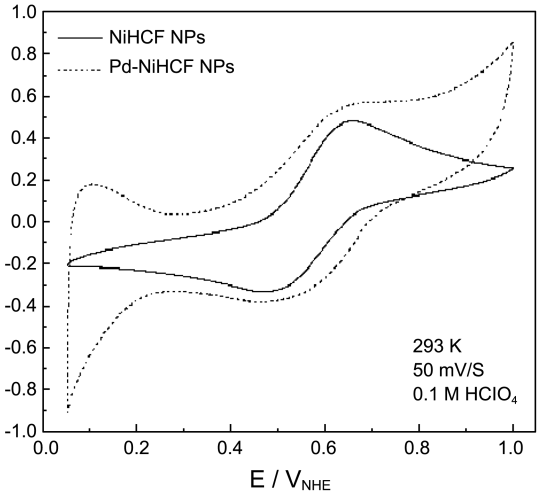

Figure 3. Cyclic voltammetry of NiHCF NPs and Pd-NiHCF NPs.

analysis (Figure 2(a)).[19] The binding energy of Pd was obtained to verify the existence of Pd loaded on NiHCF. In X-ray absorption near edge structure (XANES) analysis, identical white-line intensity manifests that NiHCF does not affect electronic structure of Pd in comparison with carbon support (Figure 2(b)).[20]

Electrochemical Properties. In the cyclic voltammetry data there was a significant difference in hydrogen adsorption/desorption area between NiHCF NPs and Pd-NiHCF NPs. Due to palladium loading hydrogen adsorption/desorption peaks were detected for Pd-NiHCF NPs. The rotating disk electrode (RDE) technique was used to conduct assessment of oxygen reduction reaction in 0.1 M $HClO_4$ solution. Figure 3 compares the ORR activity between NiHCF NPs and Pd-NiHCF NPs.[21] The ORR polarization curve measurements were initiated in the positive direction from 0.15 V *vs* NHE. There was no ORR activity for pristine NiHCF NPs. In contrast, ORR activity was obtained for Pd-NiHCF NPs (Figure 4). Pd NPs are well-known for the methanol tolerance in comparison with Pt NPs. In case of direct methanol fuel cell (DMFC), cathode catalysts require methanol tolerance and ORR results due to the methanol transfer from anode to cathode.[22] The reaction of cathode catalyst with transferred methanol hinders the ORR reactivity. The methanol oxidation of Pd-NiHCF NPs and Pt NPs has been shown by ORR in 0.1 M $HClO_4$ mixed with 0.1 M CH_3OH (Figure 5). From the ORR profile of Pt NPs the onset potential of methanol oxidation occurs at 0.33 V. However, Pd-NiHCF NPs ORR profile shows that Pd-NiHCF NPs do not react with methanol.

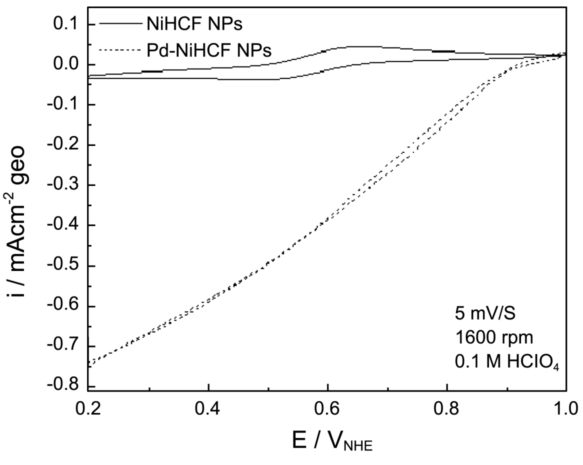

Figure 4. Oxygen reduction reactions of NiHCF NPs and Pd-NiHCF NPs.

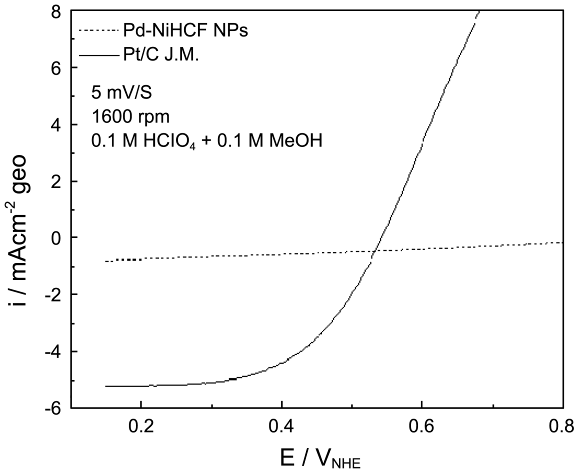

Figure 5. Methanol oxidation reactions of Pd-NiHCF NPs and Pt/C.

Conclusion

We have developed a simple synthetic procedure for the preparation of Pd nanoparticles loaded on NiHCF support that possess electrocatalytic activity for oxygen reduction reaction. RDE measurement shows that the oxygen reduction reaction can be obtained on Pd-NiHCF NPs catalyst in 0.1 M $HClO_4$ solution. The XANES analysis indicates that OH adsorption energy of Pd did not change between two supporting materials of carbon and NiHCF NPs. As a result, we have demonstrated for the first time the potential of NiHCF NPs as effective and inexpensive support of Pd NPs catalyst for ORR applications in DMFC.

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