Interactions between Low-Loading Pd Nanoparticles and Surface N-Functionalities and Their Effects on HCOOH Oxidation

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Abstract

Palladium (Pd)-based anode catalysts show greater activities than Pt catalysts for HCOOH oxidation. However, because of the ease of Pd oxidation, the electrocatalytic stability of Pd is not satisfactory. In the present study, 2.4-wt% Pd supported on N-functionalized carbon nanotubess (Pd/NCNTs) with high dispersion areas and narrow size distributions exhibited superior HCOOH-oxidation performance in comparison to Pd on charcoal (commercial Pd/C, 30-wt% Pd) and Pd on HNO3-treated CNTs (Pd/OCNTs). Surface characterization revealed that the interactions between Pd nanoparticles (PdNPs) and surface N-functionalities optimized local structures of the PdNPs and participated in the HCOOH oxidation by influencing the electronic properties of the PdNPs.

Manuscript submitted June 22, 2015; revised manuscript received August 20, 2015. Published September 19, 2015.

Direct-formic-acid fuel cells (DFAFCs) have recently attracted attention because of their many advantages when compared to direct-methanol fuel cells.1−3 Despite high activities in the initial stage, dehydration may occur and produce CO as a reaction intermediate when noble metals are used as the anode material.4,5 Resultant CO and carbonaceous deposits can be adsorbed on the metal surface and can inhibit further oxidation.6,7 In order to avoid CO generation and to improve the electrocatalytic stability, surfaces of supported metal particles must be electronically and geometrically modified.

Surface and subsurface electronic properties of noble metals are responsible for the ease of adsorption and dissociation of reactant molecules during reactions. The electronic properties of a metal are determined by its local atomic structure. Nanosizing a metal decreases the coordination number of its surface atoms (creating steps, kinks, and corners), shrinks its dband, and shifts its center toward the Fermi level.8−10 Moreover, the metal configuration can be modified via bonding with neighboring elements to form alloys, intermetallics, and strong metal-support interactions.11−13 Functionalities on supporting materials can participate in catalysis by influencing the electronic structures of loaded metal particles and thereby altering the adsorbing strength toward reactive intermediates. In HCOOH oxidation, metal nanocrystals with optimal size, shape, and crystallinity may influence the gas diffusion, mass activity, and resistance to CO poisoning.16−18 Nitrogen functionalities have been reported to influence electrocatalytic oxidation by improving the support conductivity and coupling with supported metal particles during reactions.15 Compared to oxygen functionalities, however, the role of interactions between metal nanoparticles and N-functionalities in HCOOH oxidation has not been discussed in as much detail. Moreover, surface catalysis raises the question of whether 20−30 wt% loadings of noble metals are always necessary for meaningful HCOOH-oxidation conversions and mechanism studies.

Herein, functionalization was first carried out on carbon nanotubes (CNTs) via oxidation in HNO3. Gaseous NH3 was then flowed over oxidized CNTs (OCNTs) in a tubular quartz reactor at 600 °C for 4 h to introduce nitrogen-containing functional groups on the CNTs (NCNTs). Using these functionalities as anchoring sites, palladium (Pd) ions were added to a solution of the functionalized CNTs for coor-

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Figure 1. (a) PdNPs supported on a nitrogen-doped carbon nanotube. The STEM-EDX element mapping displays distributions of each element. (b) STEM image of dispersed PdNPs on NCNTs. (c) HRTEM image of a PdNP on an NCNT with an inset of the fast Fourier transform.

Figure 3a shows the cyclic voltammograms (CVs) of formic-acid electrooxidation in a 0.5 M HCOOH + 0.5 M H2SO4 electrolyte solution on the Pd/NCNTs, Pd/OCNTs, and Pd/C (30 wt% Pd loading, supplied by Sigma Aldrich, St. Louis, MO) electrodes at a scan rate of 50 mV/s. As summarized in Table I, the anodic-peak current density of the formic-acid oxidation on the Pd/NCNTs electrocatalyst was 550.50 A/g at the peak potential, which was 1.70 and 2.60 times greater than the values measured for the Pd/OCNTs and Pd/C, respectively. The electrocatalytic specific activity of the Pd/NCNTs (Figure S5) was better (7.55 A/m²) than those of the Pd/OCNTs (5.79 A/m²) and the Pd/C (6.41 A/m²), indicating the improved catalytic activity of the Pd/NCNTs toward the HCOOH oxidation. To further evaluate the stability of the catalysts, chronoamperometry tests were conducted in 0.5 M H2SO4 and 0.5 M HCOOH at 0.1 V for 3600s. As shown in Figure 3b, in the first 1000s, the mass activity of the Pd/NCNTs was 76.86 A/g, while the mass activities of the Pd/OCNTs and Pd/C were both around 35.7 A/g. After another 1000s, the mass activity of the Pd/NCNTs was 45.60 A/g, which was still a greater value than those of the Pd/OCNTs and the Pd/C.

Pd-based electrocatalysts suffer from poor durability for formic-acid oxidation in DFAFCs, although they demonstrate greater catalytic activity. Accordingly, the stability of the catalysts was further evaluated via continuously scanning the CV curves to follow the changes in the anodic-peak current density as a function of the cycle number, as shown in Figure 4. Figure 4d shows the changes in the anodic current density for formic-acid oxidation on the three catalysts with 50 cycle numbers. As can be seen in this figure, the Pd/NCNTs catalyst showed better stability than either the Pd/OCNTs or the commercial Pd/C.

CO-stripping measurements are normally used to estimate the EASA of Pd-based catalysts. For this purpose, the specific EASA was calculated according to the following equation:

\[ \text{EASA} = \frac{Q}{mC} \]

where \( Q \) is the charge of the CO-desorption electrooxidation, \( m \) is the loaded amount of Pd, and \( C \) (420 \( \mu \)m/cm²) is the charge required for adsorption of a CO monolayer.

Figure S6 shows the CO-stripping measurements of the Pd/NCNTs, Pd/OCNTs, and Pd/C before and after 50 CV cycles. The initial EASA values were 55.96 m²/g for the Pd/OCNTs, 32.76 m²/g for the Pd/C, and 73.15 m²/g for the Pd/NCNTs (Figure S6). After 50 continuous CV cycles, the EASA value of the Pd/NCNTs remained about 34.99% of the original EASA value, while those of the Pd/OCNTs and Pd/C were 27.19% and 22.40%, respectively. Table I lists the main electrocatalytic properties of the Pd/NCNTs, Pd/OCNTs, and Pd/C. These results again indicated the enhanced activity and durability of the Pd/NCNTs.

Ammonolysis treatment modified both the structural and surface aspects of the OCNTs. High-temperature annealing in a reducing atmosphere upgraded the graphitic degree by healing the previously created defects on the OCNT walls. In turn, the conductivity of the carbon networks was enhanced, and the O-functionalities were reduced. Meanwhile, N-functionalities were introduced on the CNT surfaces. Previously, HCOOH reactivity in electrocatalysis has been correlated with the particle-size effect.24,25 It has been reported that the bond strength of the COOH-intermediate adsorption on the nano-sized Pd surfaces could be weakened, resulting in an increase in the rate of formic acid oxidation to CO2 (and in the associated oxidation current).24 In the present work, the high density of surface functionalities revealed via XPS gave rise to a strong anchoring effect toward salt precursors. After metal ions coordinated with oxygen and nitrogen
with non-equilibrium shapes and a large number of low-coordination sites (shown in Figure 1) were crucial for HCOOH oxidation with high activity.

In electrocatalysis, high activities have been reported to appear in association with low stabilities in HCOOH oxidation due to the high bond strength of the COOH-intermediate adsorption and the increased oxidation rate to CO. When we considered the metallic Pd\(^0\) as the only active phase, it should have been quickly deactivated due to its high activity, as was the case for Pd/C. In contrast, we observed high activity with improved stability on the Pd/NCNTs. When we compared the Pd/NCNTs to the Pd/OCNTs via XPS analyses, the phases of the Pd\(^0\) and the Pd-salt precursors on the Pd/NCNTs were similar to those of the Pd/OCNTs. Moreover, the size distribution and structural information of the PdNPs on the NCNTs were similar to those of the PdNPs on the OCNTs. Therefore, the XPS observation of the Pd–N bonds at 337.6 eV and the shift of the peaks on the Pd/NCNTs might have explained the obtained catalytic differences that the bonded PdNPs on the NCNTs had been a part of in the active

### Table I. Comparison of the electrocatalytic properties of the Pd/NCNTs, Pd/OCNTs, and Pd/C.

| Sample | EASA (m\(^2\) g\(^{-1}\)) | Mass activity (A g\(^{-1}\)) |
|--------|--------------------------|-------------------------------|
| 30% Pd/C initial | 32.76 | 211.4 |
| 30% Pd/C after 50 cycles | 7.35 | 63.4 |
| Pd/OCNTs initial | 55.96 | 370.9 |
| Pd/OCNTs after 50 cycles | 15.22 | 138.7 |
| Pd/NCNTs initial | 73.15 | 550.5 |
| Pd/NCNTs after 50 cycles | 25.60 | 308.7 |
phases during HCOOH oxidations. When Pd interacted with the N-functionalities, electron donation took place on the Pd. (Pd) with its low 3d-electron density does not easily bind to the COOH intermediate, so the surface (COOH)\textsubscript{ads} coverage is reduced.) Accordingly, HCOOH was easily oxidized through the direct pathway.\textsuperscript{24}

**Experimental**

CPR24-ps carbon nanotubes were purchased from Pyrograf Products Inc. (OH, USA). An FEI aberration-corrected Titan 80-300 transmission electron microscope was employed to conduct structural and chemical investigations in both the TEM and STEM modes. EDX-spectrum elemental maps were acquired in the STEM mode. XPS analyses were performed on a Thermo ESCALAB 250 instrument using monochromatic Al K\textsubscript{α} radiation with 1486.6 eV, operating at 150 W. The Pd content of each sample was measured with an inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinElmer Optima 8000). For detailed experimental information, please see the supporting material.

**Conclusions**

Palladium with a 2.4 wt% loading was supported on NCNTs with large dispersion areas and narrow particle-size distributions. The optimal sample configuration, in turn, provided us opportunities to determine the active phases during the HCOOH oxidation due to its improved homogeneity. Conventional high loadings with large structural varieties may compromise applied characterization approaches and hinder reaction-pathway studies. Sample handling in terms of functionalization, impregnation, and reduction is crucial to establish the metal-support interactions to bridge the gap between catalyst configuration and catalytic performance. In the present work, N-functionalized CNTs not only provided a platform for anchoring PdNPs with optimal structures during sample preparation but also participated in the catalysis by influencing the electronic properties and stabilities due to the interaction between the functionalities and the PdNPs.

**Acknowledgments**

This work was financially supported by the Shanghai Education Commission Scientific Research Innovation Program (No. 11YZ196), the Shanghai Key Laboratory of Materials Protection and Advanced Materials in Electric Power, and the National Natural Science Foundation of China (No. 21403137). This work was also supported by the Science and Technology Commission of Shanghai Municipality (No. 14DZ2261000).
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