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Oxygen Reduction Activity of Pt$_x$Ni$_{1-x}$ Alloy Nanoparticles on Multiwall Carbon Nanotubes

Junhyung Kim, Seung Woo Lee, Christopher Carlton, and Yang Shao-Horn$^*$$^,$z

Electrochemical Energy Laboratory and Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

Pt$_x$Ni$_{1-x}$ nanoparticles (PtNi: 1:0, 4:1, 3:1 and 0:7:1) of ~5 nm, were synthesized on carboxylic acid-functionalized multiwall carbon nanotubes (Pt$_x$Ni$_{1-x}$ NPs/MWNTs). The oxygen reduction reaction (ORR) activity measurements in 0.1 M HClO$_4$ showed an activity order of Pt$_{0.7}$Ni$_{0.3}$/MWNTs < Pt$_{0.7}$Ni$_{0.3}$/NPs/MWNTs < Pt$_{0.7}$Ni$_{0.3}$/NPs < Pt$_{0.7}$Ni$_{0.3}$/NPs/MWNTs, where Pt$_{0.7}$Ni$_{0.3}$/NPs/MWNTs had mass activity 2.5 times higher than a commercial 46 wt % Pt/C catalyst. The enhanced ORR activity of Pt$_{0.7}$Ni$_{0.3}$/NPs relative to Pt NPs could be attributed to reduced coverage of oxygenated species on surface Pt sites as evidenced by the positive shift in the onset voltage for OH adsorption.

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Experimental

For the synthesis of Pt$_x$Ni$_{1-x}$ alloy NPs on MWNTs, we utilized carboxylic group-functionalized MWNTs.24 Commercial pristine MWNTs (NANOLAB) were refluxed in concentrated H$_2$SO$_4$/HNO$_3$ (3/1 v/v, 96 and 70%, respectively) at 70°C to prepare carboxylic-acid-functionalized MWNTs, and then washed by Milli-Q water.

Among electrochemical energy conversion devices, proton exchange membrane fuel cells (PEMFCs) have been at the forefront as promising energy sources for automotive applications.1,2 However, the major challenge of PEMFCs is the kinetically sluggish oxygen reduction reaction (ORR) on Pt-based catalysts at the cathode, which limits the efficiency and contributes to the high cost of this technology.3 Fundamental studies of Pt alloy bulk surfaces show that Pt alloy surfaces can exhibit ORR activity higher than Pt.4–8 For example, Pt can segregate in the outermost layer on bulk Pt alloy surfaces to form a “sandwich-segregation”9,10 or “Pt-skin structure,”8 which is shown to weaken the bond strength to oxygenated species relative to pure Pt (Refs. 5 and 7–11) and increase specific ORR activity. Following this concept, researchers have shown that the Pt$_x$Ni (111) surface with Pt segregation to the top surface exhibits ORR specific activity 10 times greater than Pt (111).7 Remarkable progress toward fundamental understanding of ORR activity descriptor12–14 and very high activity established on single crystal surfaces has motivated recent research in developing highly active Pt$_x$M nanoparticles (NPs) with sizes of practical relevance.15–17 For example, Wu et al.16 and Zhang et al.17 have synthesized truncated-octahedral Pt$_x$Ni$_{70}$ catalysts of 6 nm, and Pt$_x$Ni nanocrystals of ~10 nm terminated with {111} facets by organic routes, which show mass ORR activity of 0.53 A/mgPt and 0.11 A/mgPt at 0.9 V vs. RHE without iR correction at room temperature, respectively.

Carbon nanotubes having high electric conductivity and high chemical stability,18 are a promising support for these highly active alloy nanoparticles for PEMFC cathode.19,20 Although previous studies21–23 have shown that Pt-alloy NPs can be synthesized on CNTs for ORR, detailed ORR activity analysis of Pt-alloy NPs on alloy nanoparticles for PEMFC cathode.19,20 Although previous studies21–23 have shown that Pt-alloy NPs can be synthesized on CNTs for ORR, detailed ORR activity analysis of Pt-alloy NPs on CNTs has not been reported. In this letter, we report a simple aqueous electrochemical technique for the synthesis of a Pt$_x$Ni$_{1-x}$/MWNTs catalyst.

The prepared 20 mg carboxylic-functionalized MWNTs were dispersed in Milli-Q water (15 ml) and PtCl$_4$ (15.5 mg in 20 ml H$_2$O) and NiCl$_2$ (12.2 mg in 20 ml H$_2$O) were introduced into the dispersed solution under vigorous stirring for 1 h, anchoring metal salts onto the carboxylic-functionalized MWNTs support via an electrostatic interaction. The mixed solution was reduced in an ice bath (4°C) for 30 min by NaBH$_4$ (0.037 g in 10 ml H$_2$O) and Pt$_{1-x}$Ni$_x$/NPs/MWNTs catalyst was synthesized by filtration and further washed thoroughly with Milli-Q water. The atomic ratios (Pt:Ni; 1:0, 4:1, 3:1 and 0:7:1) of the Pt$_x$Ni$_{1-x}$/NPs/MWNTs were controlled by PtCl$_4$ and NiCl$_2$ feed ratios. Direct current plasma-atomic emission spectroscopy (DCP-AES) was used to analyze the weight loading of Pt and Ni on the MWNTs using a Beckman spectra Span VI DCP-AES instrument at Luvac INC. Transmission electron microscopy (TEM) imaging was performed to determine particle size distributions at 200 keV on a JEOL 1010 electron microscope equipped with a field emission gun. Energy dispersive spectroscopy (EDS) was used to analyze the atomic ratio of Pt:Ni.

Freshly prepared Pt$_{1-x}$Ni$_x$/NPs/MWNT samples were dispersed in Milli-Q (18 MΩ) water via ultrasonicator (Sonic & Materials, Inc) for ORR activity measurement. Uniform, thin film electrodes were prepared on the glassy carbon electrode (5 mm in diameter) by dropping 20 μl of suspension of Pt$_{1-x}$Ni$_x$/NPs/MWNT. After evaporation of water, 10 μl of a dilute Nafion® solution (0.025 wt %), which was prepared from 5 wt % Nafion® solution (Ion Power, Inc.) was dropped on the electrodes. The saturated calomel electrode (SCE) potential scale was calibrated with the reversible hydrogen electrode (RHE) scale via H$_2$ electro-oxidation reaction. Cyclic voltammetry (CV) of Pt$_{1-x}$Ni$_x$/NPs/MWNT samples was performed in 0.1 M HClO$_4$ electrolyte at room temperature under an oxygen-free condition obtained by bubbling ultra-high purity Argon gas for at least 30 min. CV cycling was continued until steady state was reached with the potential range between 0.05 and 1.1 V vs. RHE at a scan rate of 50 mV/s. Pt electrochemically active surface area (ESA) was calculated from the charge associated with hydrogen under-potential deposition on Pt (210 μC/cm$^2$) after double layer current subtraction in the potential range between ~0.05 and ~0.4 V vs. RHE.25 The ORR activity of Pt$_{1-x}$Ni$_x$/NPs/MWNT samples was measured by sweep voltammetry in O$_2$-saturated HClO$_4$ using a rotating disk electrode at room temperature. After the electrolyte was purged with pure O$_2$ for at least 30 min, polarization curves were recorded between 0.1 and 1.1 V (RHE) at a scan rate of 10 mV/s. The Pt specific kinetic activity (j, mA/cm$^2$/pct) of Pt$_{1-x}$Ni$_x$/NPs/MWNTs was calculated from Koutecky–Levich analysis with background current subtraction and Pt ESA. The Koutecky–Levich plots based on $\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} = \frac{1}{j_k} + \frac{1}{BC_{0.5}}$ at 0.35, 0.65, and 0.75 V revealed an excellent linear behavior between 1/j and 1/BC$_{0.5}^{1/2}$. The slope, 1/BC$_{0.5}$, reflects the number of electrons involved in the reaction, which were found to be 0.177, 0.160 and 0.175 mA cm$^{-2}$ per 1/2 for TKK Pt/C, and...
PtNPs/MWNTs and Pt3Ni NPs/MWNTs, respectively. They are in good agreement with the predicted value $(0.1505 \text{ mA cm}^{-2})$ from the relationship:

$$j_D = 0.2 n F C_{O_2} (D_{O_2})^{1/2} \nu^{1/2} \sigma^{1/2} \eta,$$

where $n$, the apparent number of electrons transferred in the reaction, is equal to 4, $F$ is the Faraday constant, $C_{O_2}$ is the $O_2$ concentration in 0.1 M HClO$_4$ $(1.26 \times 10^{-3} \text{ mol l}^{-1})$, $D_{O_2}$ is the diffusivity of $O_2$ $(1.93 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1})$ in dilute electrolyte solutions and $\nu$ is the kinematic viscosity of the electrolyte $(1.009 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1})$. Knowing ORR on both Pt and Pt$_x$Ni$_{1-x}$ nanoparticles occurs via a 4-electron pathway, the specific activity was calculated from $j_D$ at 0.9 V vs. RHE. The ORR activity with $iR$ correction corrected the uncompensated ohmic electrolyte resistance ($\sim 35 \Omega$) measured via high frequency ac impedance in O$_2$-saturated 0.1 M HClO$_4$ by the following equation: $E_{iR\text{-corrected}} = E_{\text{applied}} - iR$, where $i$ is ORR current and $R$ is the uncompensated ohmic electrolyte resistance.

### Results and Discussion

Transmission electron microscopy (TEM) imaging showed that all the Pt$_x$Ni$_{1-x}$ NPs/MWNT samples had an average particle size of $\sim 5$ nm $(\pm 0.7 \sim 0.8 \text{ nm, standard deviation})$ (Fig. 2). Direct current plasma-atomic emission spectroscopy (DCP-AES) analysis showed that atomic compositions of Pt$_x$Ni$_{1-x}$ NPs/MWNTs...
are 78:22% (Pt:Ni) for Pt3Ni NPs/MWNTs, 72:28% (Pt:Ni) for Pt3Ni NPs/MWNTs, and 39:61% (Pt:Ni) for Pt0.7Ni NPs/MWNTs, respectively. Energy dispersive spectroscopy (EDS) was used to further verify the atomic Pt/Ni ratios of Pt3Ni NPs/MWNTs, which were collected and quantified using the INCA software (version 4.08, Oxford instruments). Quantification of atomic Pt/Ni ratios was performed using the Pt-L and Ni-K peaks with the sensitivity factors from the software. EDS of a large number of Pt3Ni NPs was performed by spreading the beam in TEM mode and revealed that an average atomic composition of 70:30% (Pt:Ni), which is in good agreement with (DCP-AES) analysis (72:28%). In addition, scanning transmission electron microscopy (STEM) EDS analysis with a nominal beam size of 0.7 nm showed that five randomly selected Pt3Ni alloy NPs consisted of 67–72% Pt.

Cyclic voltammetry (CV) was used to determine the ESA of Pt NPs. Figure 3a shows representative cyclic voltammograms of Pt3Ni NPs/MWNTs, Pt NPs/MWNTs and commercial TKK Pt/C electrodes (Fig. 3a). The specific surface area (32 m²/gPt) of Pt3Ni NPs/MWNTs is in agreement with the estimated value of ~40 m²/gPt, based on a surface Pt atomic percentage of 70% and a d(111) of ~5 nm of Pt3Ni NPs/MWNTs obtained from the particle size histogram.

We examined the ORR activity of Pt3Ni NPs/MWNTs using a rotating disk electrode in O₂-saturated 0.1 M HClO₄ at room temperature. ORR polarization curves of each sample were collected at different rotation rates in the range from 100 to 2500 rpm, from which ORR kinetic current in the positive-going sweep was extracted from the Roughtey-Levich equation. Figure 3b shows representative ORR polarization curves of Pt3Ni NPs/MWNTs, Pt NPs/MWNTs, and TKK Pt/C electrodes at 1600 rpm. Intrinsic ORR activity based on the Pt ESA of Pt3Ni NPs/MWNTs was compared with that of TKK (Pt/C) as a function of potential in Fig. 3c. The Pt3Ni NPs/MWNTs show the highest intrinsic activity among the catalysts, increasing in the order from Pt/C (TKK, 0.36 mÅ/m²/cm² Pt) to Pt3Ni NPs/MWNTs (0.84 mA/cm² Pt), which is three times greater than that of 46 wt % Pt/C (TKK, 2.0 mA/cm² Pt) and 27.9 μA/cm² (55 wt % Pt NPs/MWNTs) at 0.9 V vs. RHE. (b) oxygen reduction polarization curves collected from a positive-going potential sweep at a 10 mV/s scan rate at room temperature, (c) ORR intrinsic activity as a function of iR-corrected potential obtained at 1600 rpm after background and iR correction (ohmic electrolyte resistance of ~35 Ω) and (d) ORR specific (black) and mass (blue) activity of TKK and Pt3Ni NPs/MWNTs from 1600 rpm in O₂-saturated 0.1 M HClO₄, where the error bars represent standard deviations obtained from three independent measurements.

Table I. ORR specific and mass activity at 1600 rpm, 0.9 V (RHE), 0.1 M HClO₄; without and with iR-correction.

|       | jₒ (mA/cm²|Pt|) | jₘ (A/mgPt) | jₒ (mA/cm²|Pt|) | jₘ (A/mgPt) |
|-------|----------|---|------------|----------|------------|
| TKK   | 0.23 ± 0.02 | 0.22 | 0.36 ± 0.02 | 0.34 ± 0.02 |
| Pt NPs/MWNTs | 0.50 ± 0.08 | 0.10 ± 0.01 | 0.84 ± 0.19 | 0.17 ± 0.04 |
| Pt0.7Ni NPs/MWNTs | 1.24 ± 0.19 | 0.19 ± 0.01 | 1.32 ± 0.19 | 0.28 ± 0.03 |
| Pt3Ni NPs/MWNTs | 0.92 ± 0.05 | 0.40 ± 0.05 | 2.67 ± 0.60 | 0.85 ± 0.15 |
| Pt0.7Ni NPs/MWNTs | 0.90 ± 0.20 | 0.23 ± 0.07 | 1.33 ± 0.22 | 0.34 ± 0.09 |
be explained by modification of the electronic structure of Pt (5d orbital vacancies) by introducing Ni, which can reduce binding energy of oxygen containing species (OH and/or O) on surface Pt of Pt$_{3}$Ni NPs/MWNTs. The onset potential (Fig. 3a) for the adsorption of oxygenated species on the surface of Pt$_{3}$Ni NPs/MWNTs was shifted positively by ~30 mV as compared to that of Pt NPs/MWNTs, indicating weak chemical adsorption of OH$_{ads}$.

The intrinsic activity of Pt$_{3}$Ni NPs/MWNTs without iR-correction (1.24 ± 0.19 mA/cm$^{2}$Pt) is comparable to other Pt$_{3}$Ni (Ref. 35) and Pt$_{3}$Co (Ref. 36) alloy NPs catalysts reported previously. The mass activity of Pt$_{3}$Ni NPs/MWNTs was 0.85 A/mgPt, which is 2.6 times higher than that of TKK (Pt/C, 0.33 A/mgPt) at 0.9 V$_{IR}$ due to the geometric and/or electronic effects. The most active Pt$_{3}$Ni NPs/MWNTs were found to have specific (2.67 mA/cm$^{2}$) and higher than single-wall carbon nanotubes supported 2–5 nm Pt NPs (0.24 A/mgPt),37 10 nm cube Pt$_{3}$Ni NPs/MWNTs (1.32 mA/cm$^{2}$),36 and higher than single-wall carbon nanotubes supported 2–5 nm Pt NPs (0.24 A/mgPt),37 10 nm cube Pt$_{3}$Ni nanoclusters (0.11 A/mgPt) (Ref. 16) and 4 nm Pt$_{3}$Ni/Vulcan (0.09 A/mgPt).34

Conclusions

In conclusion, we utilized carboxylic acid-functionalized MWNTs as a support for Pt$_{3}$Ni NPs to investigate ORR activity in 0.1 M HClO$_{4}$ at room temperature. The ORR activity increased in the order of Pt NPs/MWNTs (0.84 mA/cm$^{2}$Pt) < Pt$_{3}$Ni NPs/MWNTs (1.32 mA/cm$^{2}$Pt) < Pt$_{2}$Ni$_{1-x}$NPs/MWNTs (1.33 mA/cm$^{2}$Pt) < Pt$_{3}$Ni NPs/MWNTs (2.67 mA/cm$^{2}$Pt), all of which are higher than Pt/C (TKK, 0.36 mA/cm$^{2}$Pt). This trend can be attributed to the inhibition of Pt-OH$_{ads}$ formation on Pt active site for ORR due to the geometric and/or electronic effects. The most active Pt$_{3}$Ni NPs/MWNTs were found to have specific (2.67 mA/cm$^{2}$Pt with IR correction) and mass activity (0.85 A/mgPt with IR correction) among the highest for Pt alloy NPs reported to date.

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