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Publisher's version / Version de l'éditeur:

<https://doi.org/10.1021/acs.chemmater.7b04221>

Chemistry of Materials, 29, 21, pp. 9579-9587, 2017-10-17

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Ultrathin Carbon-Coated Pt/Carbon Nanotubes: A Highly Durable Electrocatalyst for Oxygen Reduction

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S Supporting Information

ABSTRACT: Nanostructures constituted of Pt nanoparticles (NPs) supported on carbon materials are considered to be among the most active oxygen reduction reaction (ORR) catalysts for fuel cells. However, in practice, the usage of such ORR catalysts is limited by their insufficient durability caused by the low physical and chemical stability of Pt NPs during the reaction. We herein present a strategy to synthesize highly durable and active electrocatalysts composed of Pt NPs supported on carbon nanotubes (CNTs) and covered with an ultrathin layer of graphitic carbon. Such hybrid ORR catalysts were obtained by an interfacial in situ polymer encapsulation–graphitization method, where a glucose-containing polymer was grown directly on the surface of Pt/CNTs. The thickness of the carbon-coating layer can be precisely tuned between 0.5 nm and several nanometers by simply programming the polymer growth on Pt/CNTs. The resulting Pt/CNTs@C with a carbon layer thickness of ~0.8 nm (corresponding to ~2–3 graphene layers) showed high activity, and excellent durability, with no noticeable activity loss, even after 20 000 cycles of accelerated durability tests. These ultrathin carbon coatings not only act as a protective layer to prevent aggregation of Pt NPs but they also lead to better sample dispersion in solvent which are devoid of aggregates, resulting in a better utilization of Pt. We envision that this polymeric nanoencapsulation strategy is a promising technique for the production of highly active and stable ORR catalysts for fuel cells and metal–air batteries.

INTRODUCTION

Proton exchange membrane (PEM) fuel cells are one of the most promising clean energy devices to convert chemical energy into electricity via a sustainable process.^{1–4} However, their performance is highly dependent on the sluggish kinetics of the cathodic oxygen reduction reaction (ORR) process, which itself is determined by the efficiency of the electrocatalyst.^{5–7} Platinum (Pt) nanoparticles (NPs) dispersed on carbon materials are currently considered as the best ORR catalysts.^{8,9} Despite their popularity, there are still many issues that are yet to be addressed before reaching large-scale commercial implementation. Notably, the insufficient stability of such Pt catalyst significantly curtails the lifetime and durability of PEM fuel cells. On the other hand, in direct methanol fuel cells (DMFCs), methanol can diffuse from anode to cathode through the membrane, which can lead to cathode depolarization and thus to a significant reduction of the overall cell potential due to the methanol oxidation reaction on Pt.^{10,11} Thus, extending the lifetime and enhancing methanol tolerance of the cathode catalyst without reducing its activity and without

considerably increasing its cost remains a critical issue in the development of PEM fuel cells.

In PEM fuel cells, the ORR catalyst operates under harsh conditions (highly positive potentials and strongly acidic media) and the electrochemical surface area (ECSA) of Pt is lost during cycling, due to Ostwald ripening, dissolution and aggregation of the Pt NPs, as well as the corrosion and oxidation of the carbon support.¹² One of the effective strategies to improve the durability of Pt catalysts is to employ novel supporting materials.¹³ For example, hollow core–mesoporous shell carbon,¹⁴ mesoporous carbon,¹⁵ ordered hierarchical nanostructured carbon,¹⁶ colloid-imprinted carbon supports,¹⁷ graphene,^{9,18} and carbon nanotubes (CNTs)^{19–21} have been examined as alternatives to Vulcan XC-72, a commercial carbon black which is often used as benchmark support.²² Among those, CNTs have shown encouraging

Received: October 6, 2017

Revised: October 16, 2017

Published: October 17, 2017

Scheme 1. Synthetic Process of Pt/CNTs@C and the Corresponding Reaction at Each Step

results that have been correlated with their high conductivity, high surface area, and excellent chemical resistance.^{19,21}

Another successful strategy consists of protecting the Pt NPs in a shell.^{11,23–33} With the help of this protective layer, the Pt NPs are less prone to agglomerate or to detach from the support under highly oxidizing conditions. Among those, carbon shells have shown to prolong the catalyst life-time,^{11,24,26,28,29,33,34} but with highly variable results which can be explained by the fact that too thin carbon-coating layers are not effectively protecting the Pt NPs while too thick ones are blocking the effective active surface of Pt.²⁸ In this report, we designed a highly durable and active ORR catalyst by combining the excellent properties endowed by CNTs as support and the protective action of ultrathin graphitic carbon layers with controlled thickness. Thus, Pt NPs supported on CNTs and encapsulated in carbon layers (Pt/CNTs@C) were prepared by a facile in situ polymeric encapsulation–graphitization method which allowed precise control over carbon thickness as well as a solid anchoring of the Pt NPs at the surface of the CNTs (Scheme 1). Electrochemical evaluations indicate that the electrocatalytic activity strongly depends on the thickness of the carbon-coating layers. Once optimized, the thin coating around Pt/CNTs effectively inhibits the Pt catalyst aggregation or dissolution during cycling, while maximizing reagent mass transport. Thus, the Pt/CNTs@C composite combines high durability and catalytic activity in ORR. It also shows a high methanol tolerance, overcoming the loss of ORR activity of Pt/CNTs in the presence of methanol.

EXPERIMENTAL SECTION

Materials. CNTs (multiwall, several hundred nanometers in length and 15–30 nm in diameter) were purchased from Bayer. Formic acid (HCOOH, 98%), hexachloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 99.95%), 4,4'-azobis (4-cyanovaleric acid) (ABV, >75%), sodium lauryl sulfate (SDS), and styrene (99.9%) were all purchased from Sigma-Aldrich. Reversible addition–fragmentation chain transfer (RAFT) polymerization agent poly(acrylic acid)(butyl acrylate) (PABA) was synthesized previously in our laboratory.^{35–37}

Synthesis of Pt NPs Supported on Carbon Nanotubes (Pt/CNTs). Pt/CNTs were obtained by the chemical reduction of Pt precursor with formic acid (as shown in Scheme 1).³⁷ Typically, 10 mg of CNTs was dispersed in 4 mL of H_2O and mixed ultrasonically for ~1 h. Then 0.5 mL of formic acid and 2 mL of hexachloroplatinic acid

solution ($1\text{ mg}_{\text{Pt}}\text{ mL}^{-1}$) were added to the above suspension. The mixture was stirred at 80 °C for 30 min until the solution turned from golden-orange to colorless transparent. The as-prepared product was washed three times with water and collected by centrifugation. Then the Pt/CNTs (Pt: 17 wt %) were dried in a vacuum oven at 60 °C for 12 h.

Synthesis of Pt/CNTs Coated with Carbon Layer (Pt/CNTs@C). The synthesis of *N*-acryloyl-D-glucosamine (AGA) and of the RAFT agent PABA containing 10 acrylic acid units and 5 butyl acrylate units were reported previously.^{35–37} The polymer encapsulation of Pt/CNTs was achieved as follows: typically, 40 mg of Pt/CNTs and 20 mg of PABA were dispersed into 8 mL of water and sonicated with 30% amplitude for 5 min (Fisher Scientific sonic dismembrator 500, 400 W) to yield a black stable Pt/CNTs@PABA suspension. Then 10 mg of ABV initiator was added to the above solution. Meanwhile, 300 mg of AGA, 200 mg of styrene, and 10 mg of SDS were added to 8 mL of water, and the resulting emulsion was degassed with N_2 for 30 min. Then a syringe (50 mL) was filled with the emulsion and fixed to a syringe pump connected to the Pt/CNTs@PABA dispersion. The Pt/CNTs@PABA dispersion was heated at 80 °C under magnetic stirring and the monomers were added in under a N_2 atmosphere over a period of 5 h. Then the dispersion was kept at 80 °C for another 2 h to complete the polymerization. The encapsulated Pt/CNTs was collected by centrifugation and dried in a vacuum oven. The product was then heated under a N_2 atmosphere at 550 °C for 3 h.

Characterizations. Transmission electron microscopy (TEM) observations were conducted with a JEOL JEM-2100F microscope equipped with a field emission gun running at 200 kV. X-ray diffraction (XRD) patterns were recorded with Bruker D8 Advance with Cu $K\alpha$ as an X-ray source. Thermogravimetric analysis (TGA) was performed under an air atmosphere with a heating rate of 4 °C min^{-1} on a MS coupled thermogravimetric analyzer (TA Instruments TGA Q500/MS Discovery). X-ray photoelectron spectroscopy (XPS) was measured with a VG Escalab 220i-XL using Mg $K\alpha$ line as an excitation source.

Electrochemical Characterizations. An Autolab electrochemical system (Model, PGSTAT-302, Ecochemie, Brinkman Instruments) was used to characterize the electrochemical properties of the corresponding samples. In a three-electrode system, a glassy carbon rotating disk electrode was used as the working electrode, a Pt wire was used as the counter electrode, and a saturated calomel electrode was used as the reference electrode. All potentials in this study were referred to reversible hydrogen electrode (RHE). The catalyst ink was prepared as follows: 5 mg of catalyst was mixed with 50 μL of deionized water, 1650 μL of ethanol, and 85 μL of 5 wt % Nafion solution (in lower aliphatic alcohols and water) followed by 30 min of ultrasonication. Then 7 μL of the catalyst suspension was pipetted

onto the polished gas chromatograph (Pine Research Instrument, diameter 5 mm, 0.196 cm²) to maintain a Pt loading of about 20 μg_{Pt} cm⁻² for all tests. Then the working electrode was dried at ambient conditions before being immersed in a 0.1 M HClO₄ solution. The electrochemical measurements were all conducted at room temperature. Initially, 50 potential cycles between 0.04 and 1.2 V (scan rate = 100 mV s⁻¹) were completed to make sure that the surface of the working electrode was clean. Cyclic voltammograms (CVs) of all the catalysts were measured between 0.04 and 1.2 V (scan rate = 50 mV s⁻¹) in a N₂-saturated HClO₄ (0.1 M) solution. The polarization curves for the ORR on the samples were performed between 0.04 and 1.2 V (scan rate = 10 mV s⁻¹) in an O₂- or N₂-saturated HClO₄ (0.1 M) with an electrode rotation rate of 1600 rpm. Then the net Faradaic current was obtained by subtracting the voltammogram recorded under N₂ from the one recorded under O₂. Accelerated durability tests (ADT) were carried out by potential cycling in a square wave between 0.6 and 1.2 V in N₂-purged 0.1 M HClO₄ (scan rate = 200 mV s⁻¹). To calculate the ECSA of Pt, the following equation was used:

$$\text{ECSA} = \frac{Q_{\text{H}}}{m_{\text{Pt}}q_{\text{H}}}$$

where Q_{H} is the charge for hydrogen adsorption region, m_{Pt} is the weight of Pt (mg) on the working electrode, and q_{H} is constant (0.21 mC cm⁻²) corresponding to the charge required for monolayer adsorption of hydrogen on Pt surface.³⁸

RESULTS AND DISCUSSION

Preparation of Pt/CNTs@C Composite. The Pt/CNTs@C nanostructures were synthesized via an in situ polymer nanoencapsulation method, followed by a graphitization process. As presented in Scheme 1, Pt NPs are first formed at the surface of the CNTs through the reduction of H₂PtCl₆ by HCOOH (Step (i)). The encapsulation of Pt/CNTs begins with the adsorption of the PABA RAFT dispersant constituted of acrylic acid and butyl acrylate units onto the CNTs surface via noncovalent interactions. The PABA molecules adsorbed on Pt/CNTs act as spacers which obstruct the formation of π - π interactions between CNTs, allowing the uniform and stable dispersion of Pt/CNTs in water (see Figure S1 of the Supporting Information, and our previous reports).^{36,37} Afterward, upon the introduction of the monomers, an in situ growth of polymer chain occurs at the Pt/CNT surface via RAFT polymerization (Step (ii)). As the RAFT process is a so-called controlled polymerization process, the newly formed polymer extends the RAFT dispersant chain, resulting in the formation of a block copolymer. Because the active RAFT dispersant is anchored at the surface of the Pt/CNTs, the hydrophobic block constituted by the newly formed polymer can effectively grow into a continuous polymer shell encapsulating the Pt/CNTs. Because the initial dispersion of Pt/CNTs is devoid of aggregates, the encapsulation occurs in a 1:1 fashion, leading to the formation of Pt/CNT@polymer coaxial structures. Herein, a special monomer, *N*-acryloyl-D-glucosamine (AGA), was used to form the shell as it contains a glucosamine unit which is a carbon source. However, the resulting glucosamine polymer tends to desorb from the CNTs surface as it is water-soluble. Therefore, a mixture of AGA and hydrophobic styrene (S) (Step (ii)) was selected to form the copolymer shell. Because the amount of monomers (S + AGA) is much larger than the RAFT dispersant one, the asymmetric block copolymer is constituted of a long hydrophobic block, PSAGA, and a short surface-active block (the RAFT dispersant). The encapsulation process is exceedingly efficient as every Pt NP and CNT are trapped in a continuous shell of copolymer to form a Pt/CNTs@PSAGA structure (confirmed

by TEM, Figure 1, see below). The uniform glucose polymer layer laid the foundations of the next step. After being annealed

Figure 1. TEM images of Pt/CNTs (a, b) and PSAGA-encapsulated Pt/CNTs before (c, d) and after (e, f) graphitization. Inset of (f) shows the HR-TEM image of Pt/CNTs@C. (g) Corresponding Pt NP size variation of all nanohybrids at different synthetic steps. The size distributions of Pt were analyzed by randomly selecting 100 NPs to measure their diameters.

at 550 °C under N₂ atmosphere, the polymer layer was pyrolyzed into a graphitic carbon shell (Step (iii)).

Structure Characterization. The morphologies of the nanostructures at each synthetic step were investigated by TEM. Figure 1a,b shows the TEM images of the Pt/CNTs at different magnifications. Clearly, the Pt NPs are uniformly distributed at the CNTs surface. After polymer encapsulation, as shown in Figure 1c,d, a continuous and uniform polymer coating with a thickness of ~5–8 nm is formed around each CNT, and the well-separated Pt NPs are completely embedded in the polymer (Figure 1d), indicating the successful encapsulation. After thermal annealing, the polymer layer is transformed into graphitic carbon layer covering all around the Pt/CNTs (Pt/CNTs@C). As displayed in the TEM images (Figure 1e,f), no significant aggregation of Pt NPs can be observed after annealing. High-resolution TEM (HR-TEM) image (inset of Figure 1f) further shows that each Pt NP is completely covered by a continuous graphene-like carbon coating with a thickness of ~0.8 nm, corresponding to 2–3 graphene layers. The particle size of the Pt NPs was measured at each synthetic step (Figure 1g). Remarkably, the size of Pt NPs remains nearly unchanged, with a slight increase from ~2.4 to 3.6 nm due to the heat treatment. By contrast, when Pt/CNTs composite (no polymer coating) is annealed under the same conditions, the size of the Pt NPs reaches ~6.7 nm (Figure S3). These results indicate that the carbon coating is efficiently protecting the Pt NPs from the coarsening process which is usually associated with a loss of catalytic activity in ORR.

As illustrated in Scheme 1, when the amount of monomers is increased, the final copolymer chain becomes longer, resulting in a thicker carbon coating due to a higher content of glucose

Table 1. Recipe for the Synthesis of Carbon-Coated Pt Supported on CNTs with Different Thicknesses

sample	Pt/CNTs (g)	PABA (g)	ABV (g)	styrene (g)	AGA (g)	SDS (g)	C-coating thickness (nm)
Pt/CNTs@C-1	0.04	0.02	0.02	0.1	0.15	0.005	~0.5
Pt/CNTs@C-2	0.04	0.02	0.02	0.2	0.3	0.01	~0.8
Pt/CNTs@C-3	0.04	0.02	0.02	0.4	0.6	0.02	~1.5
Pt/CNTs@C-4	0.04	0.02	0.02	0.8	1.2	0.04	>2

unit. Thus, the thickness of the carbon coating can be precisely controlled by tuning the amount of added monomer.³⁴ Table 1 lists the composition of the various Pt/CNT@C composites. The samples were analyzed by TEM investigations to assess the thickness of the C coating layer. Figure 2 presents the TEM

Figure 2. TEM images of Pt/CNTs@C samples prepared using different amounts of monomers. (a–d) Images correspond to the Pt/CNTs@C-1 to -4, respectively, listed in Table 1. Insets show the HR-TEM images.

images of the corresponding Pt/CNT@C composites listed in Table 1. The average thickness of the carbon coating gradually increased from 0.5 nm (a) to ~0.8 nm (b), ~1.5 nm (c), and ~2 nm (d) as the monomer amount increased, which is consistent with the controlled nature of the RAFT polymerization. Observations by HR-TEM indicate that the carbon coating is composed of distorted graphite-like carbon segments containing between a single (a) to ~5 graphene layers (d). However, for Pt/CNTs@C-1 (a), the carbon coverage is not complete, and bare Pt surface can be observed occasionally (arrows in Figure 2a). In this case, the size of the Pt NPs is augmented during annealing (~4.5 nm in diameter, see Figure S2), which is consistent with the insufficient polymer protection.

Thermogravimetric analysis (TGA) further confirms the content of carbon coating on Pt/CNTs@C sample. Figure 3 shows the TGA curves of the Pt/CNT sample with (red) and without (black) carbon coating (~0.8 nm of thickness, Pt/CNTs@C-2). As reported, different oxidation behaviors can be observed in different structural forms of carbon,⁴⁰ and a less ordered carbon form tends to be oxidized at a lower temperature, whereas a well-graphitized structure is more

Figure 3. TGA curves of Pt/CNTs and Pt/CNTs@C with a carbon coating of ~0.8 nm (Pt/CNTs@C-2 in Table 1).

stable.³⁹ For both samples, a sharp weight loss occurred from ~450 up to 500 °C which could be assigned to the oxidation of CNTs.³⁹ For Pt/CNTs@C sample, an additional weight loss of ~6.5% appeared at the lower temperature region between 300 and 400 °C, which corresponds to the oxidation of the disordered graphene-like carbon coating. This relatively high weight loss indicates that the carbon layer not only covers the Pt NPs but also the CNTs (such layer is not visible by TEM because it is carbon over carbon).

The crystallinity of Pt/CNTs and Pt/CNTs@C was assessed by XRD. As shown in Figure 4a, both Pt/CNTs and Pt/CNTs@C composites show a well-crystallized Pt and graphitic carbon structure. The four major diffraction peaks at ~39.8°, 46.3°, 67.5°, and 81.4° correspond to the (111), (200), (220), and (311) planes of the face-centered cubic (fcc) Pt (JCPDS No. 04-0802).²⁹ The peak at ~25.5° can be assigned to the (002) diffraction of the graphitic carbon in CNTs.⁴¹ After carbon coating (red), the Pt peaks become more narrow, indicating an increase of crystallinity. A decrease of the peak intensity ratio of the graphite (002) to Pt (111) is also observed, perhaps due to the less ordered structure of carbon coating compared to CNTs, which is consistent with the TGA analysis.

Surface chemistry variations of the Pt/CNTs samples with and without a carbon coating were examined using XPS. Figure 4b shows the Pt 4f spectra of the samples before and after carbon coating. Both samples show the two typical peaks at high and low binding energy respectively corresponding to Pt 4f_{5/2} and Pt 4f_{7/2}. The Pt 4f signals can be deconvoluted into three doublets which can be assigned to the Pt⁰ state (red line), Pt²⁺ state (blue line), and Pt⁴⁺ state (green line).^{25,28} The abundance of the three oxidation states is not affected by the presence of the carbon coating, indicating that Pt remains unchanged during the coating process. However, a slight shift of ~0.2 eV of Pt to higher binding energy (BE) is detected in Pt/CNTs@C compared to Pt/CNTs. The increase in Pt BE in Pt/CNTs@C may result in slightly weaker Pt–O binding in comparison to that of Pt/CNT samples, an effect which has

Figure 4. XRD patterns (a) and XPS spectra (b) of Pt/CNTs and Pt/CNTs@C.

been reported to lead to an improvement of ORR rates by inhibiting the formation of surface Pt oxides.^{42,43}

Electrochemical Properties. Cyclic voltammetry (CV) experiments were conducted to estimate the electrochemical performance of as-prepared material and the effects of the carbon layer on the catalytic performance. During the preparation of catalyst ink, the dispersion of Pt/CNTs in water is not colloidal stable, leading to nonuniform electrodes. However, after carbon coating, a uniform dispersion of Pt/CNTs@C was readily obtained (Figure S4) which likely originates from the fact that the samples are prepared by carbonization of well-dispersed Pt/CNTs@polymer sample. As shown in Figure 5, the CV curves of all catalysts present the typical characteristic features of the monolayer hydrogen adsorption (H_{ads}) and desorption (H_{des}) on Pt surface and of the formation/reduction of Pt–OH and Pt–O groups. However, for the samples with carbon coating (b–e), the peaks of $H_{\text{ads}}/H_{\text{des}}$ are generally much lower in height and less well-defined compared with those of pure Pt/CNTs (a). With the increase of carbon-coating layer thickness (samples listed in Table 1), the intensity of the peak of H_{des} and H_{ads} is decreased (f). For Pt/CNTs@C-1, the lower activity can be ascribed to the larger Pt particle size.⁴⁴ For Pt/CNTs@C-4, the H_{des} and H_{ads} almost disappeared, indicating that the carbon layer is too thick and hinders the ORR and causes more sluggish kinetics. Besides, the Pt oxides reduction peak around 0.8 V has also nearly disappeared. By contrast, the Pt/CNTs@C-2 shows a more obvious $H_{\text{des}}/H_{\text{ads}}$ and Pt oxidation/reduction peaks

Figure 5. CV curves of different cycles on Pt/CNTs (a), Pt/CNTs@C-1 (b), Pt/CNTs@C-2 (c), Pt/CNTs@C-3 (d), and Pt/CNTs@C-4 (e). (f) CVs of the first cycle for all samples. CVs were recorded in N_2 -saturated 0.1 M $HClO_4$ (50 mV s^{-1} , room temperature.)

compared with other carbon-coated materials, revealing a higher exposed Pt surface.

The accelerated durability test (ADT) is a convenient method to evaluate the stability of the electrocatalysts in an accelerated fashion.³⁸ In Figure 5a, the catalytic performance of Pt/CNTs is deteriorated during the test, as shown by the obvious ECSA loss after 3000 cycles. In contrast, the performance of Pt/CNTs@C (b–e) is more stable. The ECSAs in the first cycles are always the smallest, which may be due to the prolonged time necessary to activate the catalyst. Once activated, the CV curves of the catalysts do not show significant change over time, suggesting that the carbon layer protects the Pt NPs during ADTs. Thus, the carbon coatings exert two antagonistic effects on the ORR as it can improve the stability, but also reduce the catalytic activity more or less, depending on the layer thickness. Therefore, precisely controlling and optimizing the carbon-coating thickness is highly desirable, yet remains a great challenge.

By integration of the charge in the hydrogen adsorption region ($0 \leq V \leq 0.3 \text{ V}$), ECSA can be estimated to evaluate the catalyst properties. After the first cycle (Figure 5f, also see Table S1), the ECSA of Pt/CNTs and Pt/CNTs@C-(1–4) are found to be 75, 33, 64, 35, and 11 m^2/g , respectively. Except for Pt/CNTs@C-1, the ECSA decreases with the increase of carbon-coating thickness because the carbon layer acts as an obstacle for the catalysis reaction. The ECSA value of Pt/CNTs@C-2 is comparable to that of Pt/CNTs, suggesting that the hindrance caused by the carbon layer in this catalyst is minimized. The low ECSA value for Pt/CNTs@C-1 is mainly attributed to the larger size of Pt NPs caused by the annealing

process at 550 °C but without sufficient carbon layer protection.

The alteration of ECSA as a function of cycle numbers is summarized in Figure 6. For Pt/CNTs, a sharp drop of ECSA

Figure 6. ECSA as a function of reaction cycles for Pt/CNTs and Pt/CNTs@C-(1–4). The values of ECSA were calculated from the H_{ads}/H_{des} charge in CVs.

takes place after 3000 cycles, with only 50% of the initial ECSA remaining. By contrast, for Pt/CNTs@C samples, no obvious changes (except for the first cycle as mentioned above) occurred after 3000 cycles of ADT. Impressively, after 1000 cycles of ADT, the ECSA of Pt/CNTs@C-2 is significantly larger (2 to 4 times) than those of pristine Pt/CNTs and other carbon-coated samples. The increase in ECSA over time for all carbon-coated samples can be attributed to the slight corrosion of the carbon layer, leading to a gradual exposition of fresh Pt surface.²⁸ Thus, a carbon-coating thickness of ~0.8 nm (Pt/CNTs@C-2, Figure 5c) offers the optimal compromise between activity and durability.

Figure 7 shows the typical ORR linear sweep voltammeters (LSVs) for all samples under identical experimental conditions. The best catalyst should exhibit the highest possible value of half-wave potential ($E_{1/2}$) and current values at 0.80 V (vs RHE) (see Table S2 for details). The sample Pt/CNTs@C-4 shows the lowest values before and after ADT testing, indicative that the carbon layer is too thick. Initially (before ADT testing), the “best” catalyst (based on $E_{1/2}$ and current value at 0.80 V) is the Pt/CNTs catalyst. However, after 3000 cycles, the trend is clearly reversed; compared to Pt/CNTs, the Pt/CNTs@C-2 shows much higher $E_{1/2}$ potential (0.84 V vs 0.76 V) and current density at 0.80 V (3.1 vs 1.4 mA/cm²). The activity of Pt/CNTs@C-2 catalyst after 3000 ADT is still lower than the initial activity of the state-of-the-art Pt/C catalyst,^{45–48} and more work is underway to improve the activity of this highly stable catalyst. Remarkably, the $E_{1/2}$ potential and current values of Pt/CNTs@C have increased during ADT testing, whereas those of Pt/CNTs decrease (by more than 50% for the current density), clearly indicating the protective role of the carbon coating. These results confirm that the Pt/CNTs@C-2 catalyst has a much better lifetime performance. In addition, the ORR performance of Pt/CNTs and Pt/CNTs@C-2 catalysts in the presence of CH₃OH are shown in Figure 7f. In the presence of methanol, there are obvious anodic peaks for methanol oxidation reaction (MOR) at around 0.8 V (vs RHE) in the ORR polarization curves for all samples. Therefore, there are competitions between the ORR and MOR for all catalysts.¹⁰ Interestingly, Pt/CNTs@C-2 shows much smaller current

Figure 7. LSVs on Pt/CNTs (a), Pt/CNTs@C-1 (b), Pt/CNTs@C-2 (c), Pt/CNTs@C-3 (d), and Pt/CNTs@C-4 (e) (before and after ADT test, 3000 cycles). (f) Pt/CNTs and Pt/CNTs@C-2 in the presence of 0.5 M methanol. LVs were recorded in O₂-saturated 0.1 M HClO₄ (10 mV s^{−1}, room temperature).

density for MOR than that for Pt/CNTs, indicating the much better methanol tolerance of the former catalyst. This is because the carbon shell could reduce/block the adsorption of methanol on the Pt surface.

TEM analyses were conducted for samples after 3000 cycles of ADT. Figure 8a shows that Pt NPs in Pt/CNTs (initial size 2.4 nm) agglomerated into irregular larger NPs of size ~11.5 nm. By stark contrast, no obvious aggregation is observed for Pt NPs in Pt/CNTs@C-2 (Figure 8b, 3.9 nm after ADT vs 3.6 nm

Figure 8. TEM images and the size distribution of Pt NPs of Pt/CNTs (a), Pt/CNTs@C-2 (b) after ADT.

before ADT). This observation is consistent with all electrochemical tests, and confirms that the Pt/CNTs@C-2 is more electrochemically stable than the unmodified Pt/CNTs catalyst. The TEM images (Figure 8) also indicate that Pt/CNTs@C is less aggregated (better dispersion in solvent) than Pt/CNTs without carbon coating. Indeed, during the polymer nanoencapsulation step, the carbon nanotubes are dispersed in water, forming a stable, homogeneous, and aggregate-free dispersion.²¹

Furthermore, we evaluated the stability of Pt/CNTs@C-2 catalyst by a continuous 20 000 potential cycling ADT test. As shown in Figure 9a,b, with cycling, the ECSA of Pt/CNTs@C-2

Figure 9. Long-term performance on CV curves of Pt/CNTs@C-2 (a) and Pt/CNTs (c). ECSA as a function of reaction cycles for Pt/CNTs@C-2 (b) and Pt/CNTs (d). CVs were recorded in N_2 -saturated 0.1 M $HClO_4$.

catalyst gradually increases due to the corrosion of the carbon coating and increased exposure active sites of Pt NPs. Interestingly, the ECSA reaches a plateau ($\sim 85 \text{ m}^2/\text{g}$) at 2000 cycles and it remains stable for 10 000 cycles, indicating the important role of carbon layer in preventing the aggregation of PtNPs. Even after extended 20 000 cycles, the ECSA is still $\sim 64 \text{ m}^2/\text{g}$ which is close to the initial ECSA, and represents only a 25% loss compared to the plateau value. In sharp contrast, the ECSA of Pt/CNTs decreases continuously over time, as shown in Figure 9c,d. Moreover, after 10 000 cycles, the ECSA of Pt/CNTs is only $27 \text{ m}^2/\text{g}$, which indicates a $\sim 64\%$ loss of its initial ECSA. In this test, Pt/CNTs@C-2 clearly demonstrates extremely high durability due to carbon coating.

On the basis of the above results, a possible mechanism for the significantly enhanced durability is proposed. In general, the size increase of the pristine Pt NPs is due to the Ostwald ripening.^{12,26} The thin carbon layer wrapped on the Pt NPs not only acts as a protective layer but also acts as a barrier between catalytic sites and reactants. The thickness of the disordered graphitic layer of carbon plays a key role in controlling the electrocatalytic performance.³⁴ A carbon coating of $\sim 0.8 \text{ nm}$ average thickness (Pt/CNTs@C-2, Scheme 2, left) is permeable to oxygen molecules without hindering the mass transport of molecular oxygen and the contact between oxygen and the catalyst surface. In addition, such carbon coating is

Scheme 2. ORR Reaction Taking Place on Pt/CNTs@C Samples with Different Carbon-Coating Layers

sufficiently thick to prevent Pt NP dissolution or detachment from the CNT surface. Furthermore, it can reduce the adsorption of methanol (the methanol molecule is too large) on the Pt surface and shows higher tolerance to methanol. While, when the carbon coating is too thick, as depicted on the right part of Scheme 2, the oxygen molecules cannot easily reach the surface of the catalyst. In this case, the carbon layer mainly works as an obstacle for ORR, therefore resulting in a lower activity of the catalyst.

CONCLUSIONS

We have developed a facile in situ polymer nanoencapsulation–graphitization method to prepare carbon-coated catalysts (Pt/CNTs@C). The thickness of the carbon coating can be precisely controlled by varying the amount of added monomer, and the optimal thickness for ORR catalysis has been explored. This in situ polymeric encapsulation–graphitization method leads to materials which are devoid of macroscopic aggregates (see Figure 1 and 8), thus overcoming the tendency of CNTs to bundle and to resist homogeneous deposition. Remarkably, after 20 000 cycles of ADT, the electrocatalytic activity of the Pt/CNTs @C sample with 0.8 nm carbon coating is comparable to the initial ECSA of Pt/CNTs before ADT cycling, demonstrating that proper carbon coating can significantly improve the stability of the Pt-based catalysts. Furthermore, it also shows a high tolerance to methanol after coating with carbon layer. As it is a facile, easily scalable, and environmentally benign approach, this polymeric nanoencapsulation strategy is a promising technique for the design of highly active and stable Pt-based catalysts for ORR in fuel cells or to other electroactive devices.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.7b04221.

Optical images of catalyst dispersions, TEM images (PDF)

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Notes

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ACKNOWLEDGMENTS

The authors would like to acknowledge funding from the Natural Sciences and Engineering Research Council of Canada and Fonds de la Recherche du Québec sur la Nature et les Technologies (FRQNT), Centre Québécois sur les Matériaux Fonctionnels (CQMF), the Canada Research Chair program. J.Z. and Q.W. would like to thank to FRQNT for the fellowship. J.Z. also thanks the funding support (17JDG008) from Jiangsu University. X.T. and Q.W. are grateful to the CSC scholarship.

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