

The real role of carbon in Pt/C catalysts for oxygen reduction reaction

Weilin Xu, Xiaochun Zhou, Changpeng Liu, Wei Xing*, Tianhong Lu

State Key Laboratory of Electro-analytical Chemistry, Changchun Institute of Applied Chemistry, Graduate School of the Chinese Academy of Sciences, 5625 Renmin Street, Changchun 130022, Jilin, PR China

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Abstract

A new electrocatalysis of carbon materials for oxygen reduction reaction (ORR) on Pt/C catalysts was discovered. It was found that there exist two kinds of electroactive sites on these supports of carbon materials, which can effectively electrocatalyze the reduction of peroxide intermediated from oxygen reduction on Pt, as this provides continuous driving force to move the equilibrium toward the production of peroxide from ORR.

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1. Introduction

The oxygen reduction reaction (ORR) has been the focus of electrochemical studies over many years especially because of its critical role in fuel cells, biochemistry, neuroscience and physiology [1–4]. In the field of fuel cells, the widely used catalysts for ORR are mainly the carbon-supported platinum (Pt) nanoparticles [5–14]. Up to now the direct ORR on different carbon materials, such as carbon nanotubes [12], glassy carbon [15], highly oriented pyrolytic graphite [16], and active carbon [17] has been extensively studied. However, due to the very high overpotential for direct ORR on these carbon materials [12,18], in all Pt/C heterogeneous catalysts for ORR, the carbon materials are only regarded as supports for metal nanoparticles [11]. In this opinion, all the catalysis of Pt/carbon catalysts for ORR was assigned to the electroactive sites of Pt simply. But is it really the truth? In 2003, Wang et al. [19] reported that the “pure” carbon nanotubes (CNTs) could effectively catalyze the reduction of peroxide (H_2O_2), which is the intermediate of ORR on Pt [4]. If it is the truth for CNTs, then the Pt/CNTs catalysts for ORR should be binary: CNTs also can electrocatalyze the reduction of perox-

ide intermediated from oxygen reduction on Pt, as this provides continuous driving force to move the equilibrium toward the production of peroxide from direct ORR on Pt. But recently Banks et al. reported [20], as the experimental condition adopted by Joseph Wang for the purification of CNTs was too gentle to completely remove the metal impurities on CNTs, that the “electrocatalysis” of CNTs observed by Joseph Wang should be attributed to the residual metal impurities, such as iron, on CNTs. But if there are no other impurities on CNTs or other carbon materials, do these carbon materials still can catalyze the reduction of peroxide?

In the following we report a new discovery about the role of carbon materials in Pt/C catalysts for ORR: besides supporting Pt nanoparticles the carbon materials are also electroactive components for ORR. Two kinds of electroactive sites on carbon materials can effectively electrocatalyze the reduction of peroxide intermediated from oxygen reduction on Pt, as this provides continuous driving force to move the equilibrium toward the production of peroxide from ORR.

2. Experimental

Single-walled carbon nanotubes (SWCNTs) and carbon nanofibres were purchased from Nanoport Co. Ltd.

* Corresponding author. Tel.: +86 431 5262223; fax: +86 431 5685653.
E-mail address: xingwei@ciac.jl.cn (W. Xing).

(Shenzhen, China) and NanoLab, Inc. Newton (MA). Carbon blacks (CB) were from Liaoyuan carbon black factory (China), Asia-pacific specialty chemicals Kuala Lumpur, USA and Cabot Corp. (Vulcan XC-72), respectively.

All the powders of CNTs, carbon nanofibres and carbon blacks purchased from different producers were purified by refluxing (80 °C) the as-received carbon materials in 2.6 M HNO₃ for 16 h and then washed with water repeatedly to ensure a complete removal of residual acid and other impurities. Pt/CNTs (40 wt% Pt) nanohybrids were prepared as the following: the acid-treated SWCNTs from Nanoport Co. Ltd. (Shenzhen, China) were sonicated in concentrated sodium dodecylbenzene sulfonate solution for 10 h, then the concentrated H₂PtCl₆ solution was added with stirring for 24 h. After that the strong alkali NaOH was added to adjust the pH value to 9. Two hours later the reducing reagent of NaBH₄ was added to reduce the metallic precursors. Then the mixture was filtrated and washed with ethanol and water repeatedly to remove impurities. Pt/XC-72 CB (40 wt% Pt) catalysts were purchased from E-TEK Company.

All the electrochemical tests (cyclic voltammograms (CVs) and linear sweep voltammograms (LSV)) were carried out with a Model 273 electrochemical workstation (USA) with a conventional three-electrode cell. The working electrode was a thin layer of Nafion impregnated catalyst or carbon powder cast on a glassy carbon disk held in a Teflon cylinder or bare smooth GC or pyrolytic graphite electrode. The GC/CNT, GC/Pt/CNT, GC/Pt/XC-72 CB or GC/ XC-72 CB electrodes were prepared as following: (i) a slurry was first prepared by sonicating the mixture

of 1 mL of alcohol, 5 mg of Pt/CNT, Pt/XC-72 carbon black, or acid-treated carbon powders, and 50 μL of Nafion solution (Aldrich, 5 w/o Nafion) for 1 h; (ii) 6 μL of the slurry was pipetted and spread on the glassy carbon disk; (iii) the electrode was then dried at 60 °C for 1 h. The poisoning of iodine (I⁰) toward electrodes was proceeded by dipping the electrodes in iodine (I⁰) saturated water solution for 5 min and then washed with deionized water for twice. A Pt foil electrode and an Ag/AgCl were used as the counter and reference electrodes, respectively. All potentials in this report are quoted against Ag/AgCl. All electrolyte solutions were deaerated by high purity nitrogen for 15 min prior to any measurement.

The energy-dispersive X-ray (EDX) analyzer is a common accessory of a LEO 1525 FE-SEM scanning electron microscope and this EDX analyzer was used to analyze the composition of the acid-treated carbon powders.

3. Results and discussion

Fig. 1 shows the typical EDX spectrum for SWCNTs (Shenzhen, China) after super-washed in 2 M HNO₃ solution for 35 h reported by Wang (A) [19,20] and after refluxed in 2.6 M HNO₃ solution at 80 °C for 16 h in our present experiments (B). Fig. 1A shows the cobalt could be observed clearly on super-washed CNTs, indicating the “super-wash” method was too gentle to remove the impurities on CNTs clear. Compared with Fig. 1A, Fig. 1B shows after being refluxed in 2.6 M HNO₃ solution at 80 °C, all the impurities, such as cobalt (Co) or sulfur, had been removed completely.

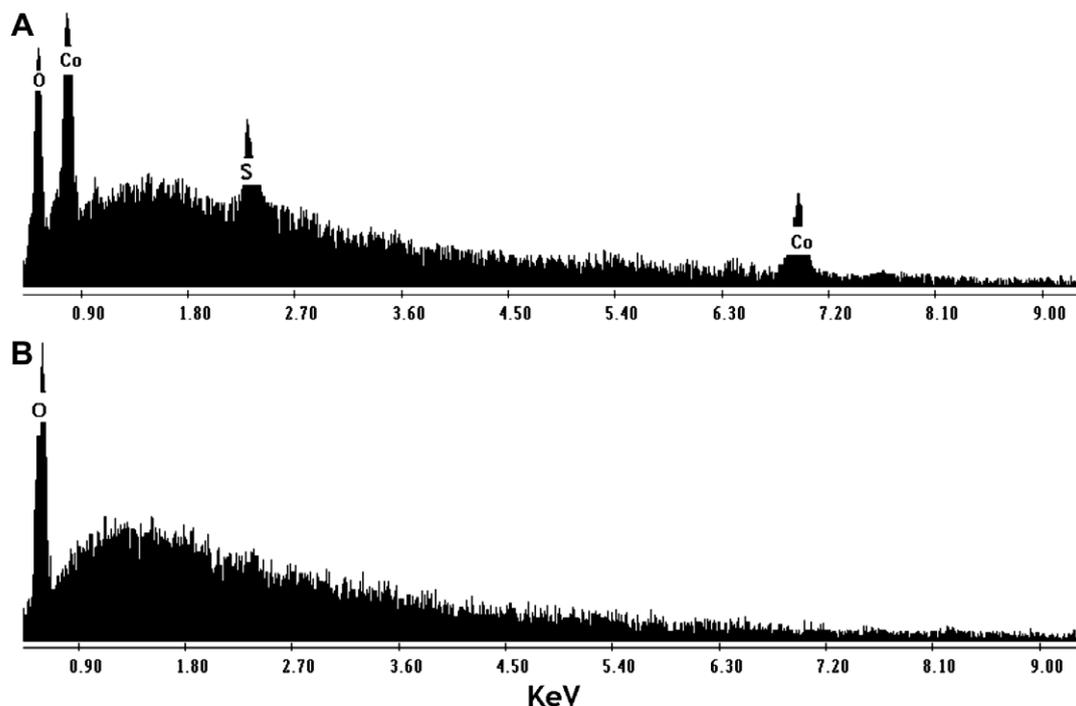


Fig. 1. ESEM-EDX spectrum of CNTs after super-washed [19] (A) and after (B) refluxed at 80 °C.

Fig. 2A shows CVs for smooth polycrystalline Pt (curve a), CNTs (curve b) and Pt/CNTs (curve c). For CNTs there is a couple of redox peaks denoted with *. According to previous work [21–25], this couple of peaks should be attributed to the redox of oxygen-containing groups or their derived functionalities on carbon surface: carboxyls [21,22], phenolic hydroxyls [22,24,25], or carbonyls [21,22]. Compared with smooth Pt (curve a in Fig. 2A), the Pt/CNTs modified electrode shows a new couple of redox peaks, which obviously correspond to the redox of oxygen-containing groups on CNTs.

Fig. 2B shows the electrocatalytic properties of Pt/CNTs for ORR. Curve a is the linear sweep voltammogram (LSV) for GC/Pt/CNTs electrode in 0.1 M H₂SO₄ solution deoxygenated by bubbling N₂. Compared with Fig. 2A, the peaks denoted with # and * should correspond to the reduction of platinum oxide and oxygen-containing groups, respectively. Curve b is the LSV result for the above electrode in 0.1 M H₂SO₄ solution saturated by oxygen. Obviously there are two large reduction current peaks. Compared with curve a, the current for # peak should correspond to oxygen reduction catalyzed by Pt. Over the # peak there is a larger catalytical current (* peak), generally which seemed to correspond to oxygen reduction electrocatalyzed by reduced oxygen-containing groups. But do these reduced groups really can electrocatalyze the direct reduction of oxygen in this potential region?

The electrocatalytic behavior of CNTs for oxygen reduction was shown on curve b in Fig. 3A. Compared with the background (curve a, dotted line), a large current for direct ORR appeared at about $E_{pc} = -0.32$ V, after performing ab initio density-functional-theory calculations and molecular dynamics simulations, Britto et al. found that the electrocatalysis of CNTs for ORR at -0.32 V should be assigned to the defects on carbon surface, such as the pentagons at tips and pentagon–heptagon defect pairs in the lattice, which are responsible for the direct oxygen reduction [12]. While in the potential window for the redox of oxygen-containing groups there is no catalytic

current. This fact shows clearly these groups could not directly catalyze the oxygen reduction. In fact Che et al. observed that CNT is inert to oxygen reduction in this potential range of oxygen-containing groups [5]. These facts tell firmly that the larger current peak on Fig. 2B(b) was caused by the reduction of intermediates from ORR instead of oxygen itself.

It is well known that the ORR in aqueous solution generally proceeds by either of the two pathways [1,2,4]. One is a direct four-electron pathway through which the molecular oxygen is directly reduced to H₂O. The other is a two-step two-electron pathway through which the molecular oxygen is reduced to H₂O₂, followed by the further reduction of it.

It was interesting to validate that the reduced oxygen-containing groups on carbon can catalyze the H₂O₂ reduction. As shown in Fig. 3A(c) (dash dot–dot line), besides a large reduction current peak at -0.32 V corresponding to the reduction of H₂O₂ catalyzed by the defects on carbon surface [12], a large reductive current also appeared in the region corresponding to the redox of oxygen-containing groups. Obviously this large current should be assigned to peroxide reduction electrocatalyzed by reduced oxygen-containing groups. In order to further validate the extensive existence of the above two kinds electroactive sites on different carbon materials, other eight typical carbon materials (CB and CNTs from different producers, pyrolytic graphite electrode, bare smooth glassy carbon (GC) electrode and carbon nanofibre) were also studied. Figs. 3B and C show the typical electrochemical and electrocatalytic behaviors of XC-72 CB and bare smooth GC electrode for the reduction of oxygen and peroxide, respectively. The similar results were also obtained on other six kinds widely used carbon materials (not shown here). All these results show the above two kinds of active sites (defects on carbon surface and the oxygen-containing groups) also exist on these carbon materials more or less. This fact validates firmly both of these two kinds of active sites on these carbon materials can effectively catalyze the

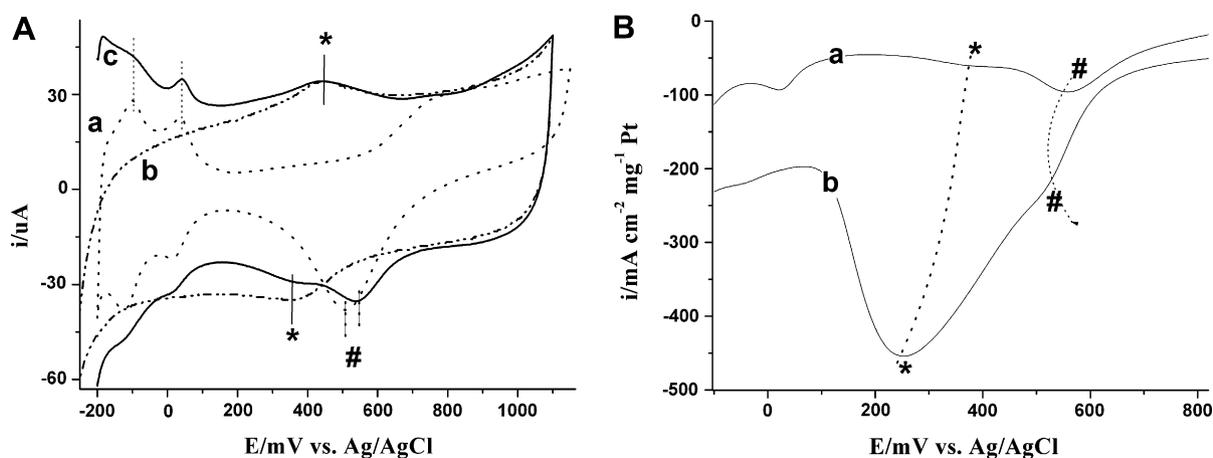


Fig. 2. (A) CVs at smooth polycrystalline Pt electrode (curve a), GC/CNTs electrode (curve b) and GC/CNTs/Pt electrode (curve c) in 0.1 M H₂SO₄; (B) LSVs: curve a and curve b are for the GC/CNTs/Pt electrode in 0.1 M H₂SO₄ and 0.1 M H₂SO₄ saturated by oxygen, respectively. Scan rate: 100 mV/s.

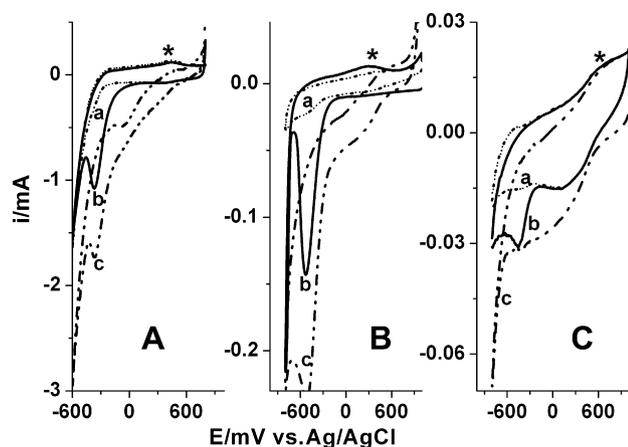


Fig. 3. CVs on GC/CNTs electrode (A), GC/XC-72 carbon black electrode (B) and GC electrode (C). Dotted lines (curve a): the background in 0.1 M H_2SO_4 solution; solid lines (curve b): in 0.1 M H_2SO_4 solution saturated with oxygen; dash dot-dot lines (curve c): in 0.1 M $\text{H}_2\text{SO}_4 + 0.2 \text{ M H}_2\text{O}_2$. Scan rate: 100 mV/s.

reduction of peroxide solely. It was also found that the CNTs are the best supports, which contain much more electroactive sites. Both the CNTs and CBs possess good application prospect due to their high activity for the reduction of peroxide.

Recently Banks et al. [20] reported the catalysis of CNTs toward peroxide reduction observed by Wang et al. [19] “in fact” came from the high-level impurity of iron, which had not been removed clear in their treatment process. While our results shown on the above imply the catalytical current observed by Wang et al. [19] in fact included two parts: one part came from the CNT itself and the other came from the promotion of the residual high-level iron toward peroxide reduction. Also the catalytic current near the * peak of Fig. 2B(b) should be assigned to the catalysis of CNT itself toward the reduction of peroxide intermediated from ORR on Pt. Cui et al. observed the large catalytic current (* peak) on Pt/CNTs catalyst for ORR, but they did not study the origin of it and only simply attributed it to the reduction of peroxide into water [26].

In order to directly observe the reduction of peroxide solely catalyzed by carbon materials in Pt/C catalysts, we found for the first time that the iodine (I^0) could completely inhibit the catalysis of Pt toward oxygen or peroxide reduction with no interferential signals as shown in Fig. 4. Compared with the background (curve 1) of pure Pt electrode, curve 2 shows the absorption/desorption of hydrogen or the redox of Pt all can be restrained completely by the adsorbed I^0 . This complex electrode of Pt- I^0 is inert to the reduction of oxygen (curve 3) or peroxide (curves 4 and 5). At the higher potential region ($>0.6 \text{ V}$), there is a high positive current due to the decomposition of peroxide into oxygen (curve 4) [27].

Further more as shown in Fig. 5A, curves a and b show that the I^0 does not affect the redox of oxygen-containing groups on CNTs. Curves c and d show the adsorbed I^0 does not affect the electrocatalysis of the two kinds of elect-

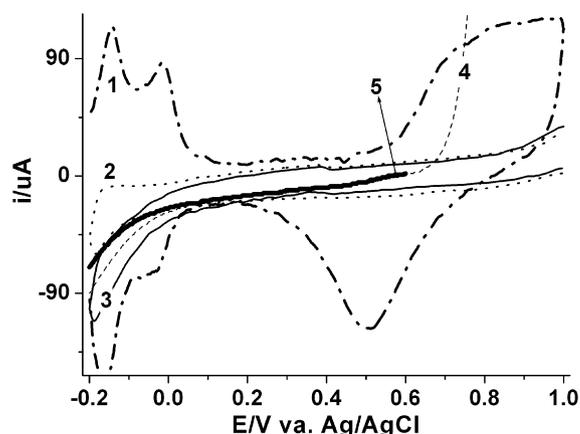


Fig. 4. CVs for smooth Pt electrode (curve 1) and Pt- I^0 (curve 2) in 0.1 M H_2SO_4 solution, Pt- I^0 (curve 3) in oxygen saturated 0.1 M H_2SO_4 solution, LSVs for Pt- I^0 ((4) and (5) curves) in 0.1 M $\text{H}_2\text{O}_2 + 0.1 \text{ M H}_2\text{SO}_4$ solution with onset potentials of 0.8 V and 0.6 V, respectively.

roactive sites toward peroxide reduction. From the above results it can be deduced firmly that the I^0 can selectively poison the Pt active sites on Pt/Carbon catalysts and then one can solely observe the electrocatalysis of carbon in Pt/C catalysts for peroxide reduction. Fortunately, as shown in Fig. 5B, after the Pt/CNTs was poisoned by iodine (I^0) both the absorption/desorption of hydrogen and the redox of Pt all were restrained and only the characteristic wave of CNT could be observed (a couple of redox peaks of oxygen-containing groups denoted with * on curve b). Curve c shows the catalysis of the Pt/CNTs- I^0 electrode toward peroxide reduction. It is consistent with that on pure CNTs shown in Fig. 3A(c). Similar results were also obtained on Pt/XC-72 CB catalysts (E-TEK Comp.) (Fig. 5C). It shows after being poisoned by I^0 , the poisoned electrode only shows the characteristic wave of pure CB. Due to the lower content of oxygen-containing groups on CB, their redox peaks were not very clear, but the catalytic currents (curves 1–3) toward peroxide reduction validate firmly the existence of the oxygen-containing groups on CB.

The smooth Pt electrode, Pt/CNTs and Pt/XC-72 CB modified GC electrodes were further investigated by rotating disk electrode for ORR and then the values of n (the numbers of electron transferred in the ORR) were evaluated from Koutecky–Levich equation to be about 3.99, 3.01 and 3.24, respectively. These results indicate that the process for ORR on Pt/C catalysts contains both four-electron and two-electron pathways and the carbon materials can greatly increase the percentage of the two-electron process compared with pure Pt. Also there is a higher percentage of the two-electron process on Pt/CNTs than that on Pt/Carbon black due to the higher concentration of the two kinds of active sites on CNTs [28,29].

On the other hand, it is well known that Pt, Pd, Ir or Os tend to catalyze the decomposition of H_2O_2 into O_2 inversely [30]. From this point of view, the two-electron process for ORR on pure Pt is negligible compared with the direct four-electron process [14,28]. However, if Pt nanoparticles

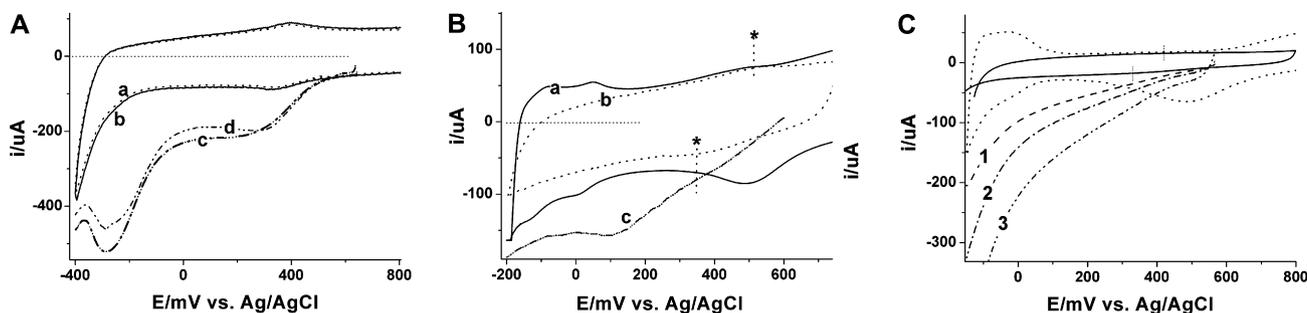


Fig. 5. (A) CVs (a and b) for the GC/CNTs and GC/CNTs/I⁰ in 0.1 M H₂SO₄ solution, the LSVs obtained in 0.15 M H₂O₂ + 0.1 M H₂SO₄ solution: GC/CNTs electrode (curve c), GC/CNTs-I⁰ electrode (curve d); (B) CVs for Pt/CNTs (curve a) and Pt/CNTs-I⁰ (curve b) in 0.1 M H₂SO₄ solution and LSV for Pt/CNTs-I⁰ (curve c) in 0.05 M H₂O₂ + 0.1 M H₂SO₄ solution; (C) CVs for Pt/XC-72 CB (dotted line) and Pt/XC-72 CB-I⁰ (solid line) in 0.1 M H₂SO₄ solution and LSV for Pt/CNTs-I⁰ in 0.1 M H₂SO₄ + 0.1 M H₂O₂ (1), 0.15 M H₂O₂ (2) and 0.2 M H₂O₂ (3) solutions.

were dispersed on carbon materials, the results would be completely different. As shown above, both the defects and the oxygen-containing groups on carbon could effectively catalyze the reduction of peroxide intermediated from oxygen reduction on Pt, as this provides a continuous driving force to move equilibrium toward the production of peroxide. Obviously this can greatly increase the electrocatalytic efficiency of Pt for ORR and the usage of oxygen. In this case, the contribution from the two-electron process for ORR will increase greatly compared with ORR on pure Pt.

4. Conclusion

In summary, it was discovered there are two kinds of electroactive sites on carbon materials, which can effectively electrocatalyze the reduction of peroxide intermediated from direct ORR on Pt, as this provides continuous driving force for ORR. These facts clarify an important fact: the Pt/Carbon catalysts for ORR are binary.

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