



# Enhanced activity and durability of the oxygen reduction catalysts supported on the surface expanded tubular-type carbon nanofiber



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## ARTICLE INFO

### Article history:

Received 29 December 2016

Received in revised form 30 April 2017

Accepted 31 May 2017

Available online 1 June 2017

### Keywords:

Carbon nanofiber

Surface modification

Oxygen reduction reaction

Fuel cell catalyst

## ABSTRACT

Tubular type carbon nanofibers (TCNFs) are prepared and used as a catalyst support material for a cathode electrode of low temperature fuel cells through structural modification. The pristine TCNF is treated by graphitization and makes partially torn-tube shape through the surface expansion by rapid thermal treatment of the oxidized graphitized TCNF. Physical properties of the TCNF group are examined, and it is confirmed that the unique ripped texture along fiber axis with graphitic structure is obtained by the surface expansion. Platinum catalysts supported on these TCNF group are prepared and evaluated. Electrochemical properties are examined via cyclic voltammograms and polarization curves for oxygen reduction reaction activity. The platinum catalyst on the surface expanded TCNF has the enhanced activity at initial and the stable performance even after accelerated durability test due to their unique structure.

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## 1. Introduction

Carbon nanofibers (CNFs) have attracted great attention as unique nanomaterials having a potential for industrial applications such as functional composites, electrochemical electrodes, semiconductor devices, electron emitters, catalysts and catalyst supports [1–6]. A number of studies on selective synthesis and structural analysis have been performed to attain uniform and controlled structure of the CNFs [7–9]. The most important factor to determine the properties of the CNF is a stacking configuration of graphene layer. The CNFs are classified into three groups as platelet (PCNF), herringbone (HCNF) and tubular (TCNF) types [10]. The graphene layers of the PCNF are stacked in the direction of perpendicular to the growth axis, so the PCNF has relatively large diameter and plenty of exposure of edge sites. The HCNF has tilted graphene layers based on the structure of the PCNF, and it leads to thinner diameter and larger specific surface area than the PCNF. The TCNF (is also known as CNT), which the graphene

layers locate the same direction of fiber axis, forms the exposure of stable basal planes on the carbon surface. The TCNF has been used as a catalyst support material due to relatively high surface area, excellent electronic conductivity, and high chemical stability. Many studies about the synthesis and application of the TCNF as a support material of platinum electro-catalyst for fuel cells, especially focusing on cathode electrode with high durability were conducted [11–13]. As mentioned above, the TCNF dominantly wrapped by stable basal plane typically has a good electrical conductivity and a robust structure caused by higher graphitic degree. Without the surface modification, however, lack of sufficient binding sites for anchoring precursor metal ions or metal nanoparticles is happened. This usually leads to poor dispersion and agglomeration of metal nanoparticles. It has a significant impact on the catalyst activity and durability. Therefore, the introduction of proper functionality onto the TCNF or structural modification is the essential ingredient for future applications.

In this presenting study, we first prepared the iron-nickel (Fe-Ni) binary catalyst and synthesized the TCNFs over the Fe-Ni catalyst from a mixture of carbon monoxide (CO) and hydrogen gases. The TCNFs were heat-treated at the temperature of graphitization to retain their robust original structure against further harsh procedure. The graphitized TCNFs were conducted additional surface modification through the expansion of graphene layer induced

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by strong oxidation and rapid heat treatment [14]. Subsequently, pristine TCNF and modified TCNFs were used as support materials for Pt/C. Electro-catalytic activities such as electrochemical surface area and oxygen reduction reaction are analyzed based on the study of the surface modification of the TCNFs. Also, we tried to evaluate the possibility as the promising support material by carrying out the accelerated durability test.

## 2. Experimental

### 2.1. Fe-Ni catalyst for TCNF

A Fe-Ni (weight ratio of Fe:Ni = 6:4) catalyst was prepared using iron nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), nickel nitrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) and ammonium hydrogen carbonate ( $\text{NH}_4\text{HCO}_3$ ). Prescribed amount of Fe and Ni agent were dissolved in 300 mL of distilled water and heated at 90 °C with stirring. When the metal nitrates were perfectly dissolved,  $\text{NH}_4\text{HCO}_3$  of 3 times of metal weight was slowly added into the mixture with vigorous stirring. The mixture was left the rest for stabilization at room temperature for 8 h, and then filtered and washed with distilled water of 4 L. The second step to prepare the Fe-Ni catalyst with nano-sized structure to enhance the catalytic activity was conducted by further heat-treatment. Pristine Fe-Ni catalyst was treated at 400 °C in air flow for 4 h to induce the slight oxidation and form the nanostructure. The reactor was cooled down under inert atmosphere and the Fe-Ni catalyst was heated for reduction at 500 °C in flow of hydrogen for 20 h. When the reactor was cooled down and attempted aging at 35 °C in air for 1 h, the prepared Fe-Ni catalysts were collected.

### 2.2. Preparation and modification of the TCNF

The TCNF was synthesized using a middle-scale vertical furnace with the capacity of 5 g per day. The Fe-Ni catalyst (0.1 g) was spread on the reaction quartz bed assisted by an acetone and then the reactor was purged with helium gas. The furnace heated up to designed temperature during 2 h. When the temperature of furnace reached synthesis condition, supplied gas was changed to helium and hydrogen mixture (volume ratio 4:1 = He:H<sub>2</sub>) for reduction of Fe-Ni catalyst for 30 min. After an atmosphere was replaced with helium for 30 min, the TCNF was synthesized from carbon monoxide and hydrogen gases (volume ratio of 1:1) over Fe-Ni catalyst for 2 h. After that, the gas mixture was re-changed with helium and hydrogen for stabilization of the TCNF for 30 min and cooled down under inert helium gas. The amount of the total reaction gas was fixed to 1 L/min. The TCNF was treated with 10 wt% hydrochloric acid (HCl) solution twice over 24 h to remove the metallic catalysts. Finally, the sample was sufficiently washed with distilled water and dried overnight at 80 °C.

Further treatment in order to obtain substantial structure called graphitization was conducted in extremely high temperature. The graphitization treatment was performed at 2800 °C in flow of argon for 10 min. The TCNF processed this graphitization referred as the G-TCNF.

A surface expansion of the G-TCNF was done through both of strong oxidation and followed rapid thermal treatment [15]. Three gram of the G-TCNF was immersed in high concentrated  $\text{H}_2\text{SO}_4$  of 98 wt% for 12 h with stirring, and then 9 g of  $\text{KMnO}_4$  was slowly added in an ice bath. The temperature of solution was carefully paid attention not to exceed 55 °C. When the  $\text{KMnO}_4$  was dissolved completely, the temperature raised up to 70 °C and stirred for 1 h. Distilled ice of 300 g and 35 wt%  $\text{H}_2\text{O}_2$  solution of 90 mL were poured into the mixture for quenching, and then the reaction was finished with vigorous stirring for 3 h. The oxidized G-TCNF slurry was separated and collected using a centrifuge with 4800 rpm, and

washed with 1 M HCl solution. The oxidized G-TCNF was completely prepared by washing with distilled water, filtration and dryness overnight. A surface expansion of the oxidized G-TCNF was conducted by rapid thermal treatment. The oxidized G-TCNF was placed onto a reaction bed in helium purged horizontal tube furnace. The temperature was rapidly elevated to 300 °C in a rate of 30 °C/min, and then the elevate speed was changed in 5 °C/min up to 900 °C. The heat-treatment at 900 °C was kept going for 3 h. During the rapid thermal treatment, the formation of water droplets was discovered due to the elimination of oxidative components in the carbon structure. After the reaction was finished and cooled down, the sample was collected and named as the EG-TCNF. All carbon samples were treated by 1 M  $\text{HNO}_3$  solution for 24 h to create the oxygen function groups on the surface.

### 2.3. Preparation of Pt catalyst supported on the TCNF group

The target loading weight of Pt and the amount of Pt/C were set as 40 wt% and 0.5 g. Pt/C was synthesized by a pH controlled polyol method using ethylene glycol (EG). Pt reagent was previously mixed with 3 times of EG. After the carbons were put into EG of 200 mL with sonication for 30 min, Pt/EG and 1 M NaOH/EG solution to transfer an alkaline. The mixture was heated at 150 °C for 3 h with reflux system, and then cooled down and stabilized for 12 h. One mole of  $\text{H}_2\text{SO}_4$ /EG was poured into the solution to adjust to the neutral pH. In sequence, the reactor was heated up to 120 °C for 3 h and stabilized at room temperature for 24 h. These Pt/C catalysts by the polyol method were finished with filtration and cleaning with distilled water.

### 2.4. Characterizations

Morphologies of synthesized and modified TCNF group were observed via a scanning electron microscope (SEM, JSM-6700F, JEOL) and a transmission electron microscope (TEM, JEM-2100F, JEOL). Oxidative resistance profiles of the TCNF group were confirmed using thermogravimetric analysis (TG, STA409PC, NETZSCH). Structural properties such as specific surface area and porosity were inspected from nitrogen adsorption-desorption profile at liquid nitrogen temperature and further calculation using BET and BJH formula. X-ray diffraction profiles were obtained using a Rigaku instrument (RINT-Ultima III) with a Cu K $\alpha$  radiation. Raman spectroscopy was performed on the Dimension-P1 Raman system with 530 nm laser wavelength.

Pt loading content of the Pt/C catalysts was found out from the amount of residual in the TG. Crystallite size of the Pt particle on the TCNF group was calculated by the Scherrer equation from the Pt (220) peak at 68° of 2-theta in the XRD pattern. The deposition of Pt particles on the TCNF group was confirmed using a field emission TEM (Talos F200X). We selected 100-particle samples from the TEM images to reveal the particle size distribution. Electrochemical activities of each catalyst were evaluated using conventional three electrode system. Mirror-polished glassy carbon with a diameter of 5 mm was used as the working electrode. A Pt coil and a silver/silver chloride electrode (SSCE) were used as the counter and the reference electrode, respectively. All of the electrode potentials were conversed with references of the reversible hydrogen electrode (RHE). A catalyst slurry was prepared by blending the catalysts of 10 mg and 5 wt% Nafion solution of 57.2  $\mu\text{L}$  in distilled water of 7.5 mL and isopropyl alcohol of 2.5 mL with vigorous stirring and sonicated for 20 min in an ice bath. Ten micro-liter of the catalyst slurry was pipetted onto the working electrode. The amount of loaded Pt on working electrode was calculated from the dry matter weight of 30 times of 10  $\mu\text{L}$  catalyst slurry referring TG data. Before the electrochemical measurement for catalytic activities, the cleaning of prepared working electrode was performed

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