High oxygen reduction activity of few-walled carbon nanotubes with low nitrogen content

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ABSTRACT

Nitrogen-containing few-walled carbon nanotubes (N-FWCNTs) with very low nitrogen content (0.56 at.%) were obtained by a process involving the coating of acid functionalized FWCNTs with polyaniline (PANI) followed by pyrolysis at high temperatures. The resulting N-FWCNTs exhibited a remarkable electrocatalytic activity for the oxygen reduction reaction (ORR), despite significantly lower nitrogen content than previously reported in literature. The N-FWCNTs performed on par or better than Pt-C in the cathode of an alkaline direct methanol fuel cell, corroborating the ORR activity observed in the electrochemical cell and exhibiting a higher methanol tolerance. Interestingly, N-FWCNTs showed a high activity for the hydrogen evolution reaction and for the hydrogen peroxide decomposition, suggesting that the active sites involved in ORR can simultaneously catalyze other reactions. This unprecedentedly high activity for such a low N-content can be explained by the exceptional accessibility for the catalytic sites located in open and porous N-doped layer surrounding the FWCNT core, along with the minimization of inactive inner volume and mass compared to larger nitrogen doped multiwalled tubes.

1. Introduction

Improving catalyst materials for the oxygen reduction reaction (ORR) is one of the main issues in the development of low temperature fuel cells. Worldwide commercialization of fuel cells still remains a challenge due to the limited resources and high cost of platinum (Pt) as well as durability issues and CO poisoning of the Pt catalysts [1,2]. Recent advances in anion exchange membrane fuel cells (AEFCs) have attracted considerable attention due to the potential use of less-expensive non-noble metal catalysts, which exhibit facile reaction kinetics in alkaline media [3,4]. Research on metal-free catalysts for ORR has thus become a very active topic in catalysis, especially with the emergence of nitrogen-doped carbon nanomaterials as one of the promising electrocatalysts. Recent research has investigated nitrogen doping of different carbon nanomaterials (CNM) such as carbon nanotubes (CNTs) [5–14], carbon nanofibers (CNFs) [15,16], graphene [17,18], mesoporous carbon [19], carbon nanocages [20], and hollow carbon nanoparticles [21]. The studies are particularly numerous for nitrogen-doped CNTs (N-CNTs) among these materials. N-CNTs can also effectively catalyze other reactions, such as decomposition of H_2S to solid sulfur, and the oxidative dehydrogenation of aromatic and alkanes [22,23]. Introducing nitrogen atoms into the CNT structure effectively modulates their chemical reactivity, electron-donor ability and electrochemical properties [24]. Nitrogen dopants can shift the Fermi level to the conduction band, causing the semiconducting CNTs to exhibit metallic properties [25]. Moreover, the addition of nitrogen to the CNT wall changes the charge distribution of the nanotube so that C atoms adjacent to N become more

positively charged, resulting in an enhanced interaction with the adsorbed molecules and lower activation barrier for their decomposition [26].

N-CNTs can be obtained by either in situ doping during the CNT synthesis, or by post-treatment of as-synthesized CNTs with nitrogen-containing precursors. During in situ doping, nitrogen atoms derived from different precursors such as transition metal macrocycles [5], ammonia [6], acetonitrile [7,11], pyridine [8,9], melamine [10] and polymers [27,28] are incorporated into the carbon network simultaneously as CNTs grows. It has been reported that the presence of metals originating from a typically metal-catalyzed synthesis process can contribute to ORR catalysis [29]. To avoid misidentifying the origin of ORR activity catalyst metal residues should be removed before electrochemical measurements. However, any acid leaching to remove metals may damage nitrogen functionalities. Post-treatment methods typically avoid this difficulty by treating already purified CNTs with nitrogen precursors; such as ammonia [11], urea [14], dicyandiamide [30], or polymers including polyaniline (PANI) [13] and polypyrrole [16].

PANI offers several advantages among nitrogen-containing polymers; it is an outstanding conductive polymer with low price, good processability, controllable and stable conductivity over a wide potential range [31–33]. Moreover, PANI conjugated groups can interact strongly with the CNT walls to provide core–shell composite structures (CNT-PANI) with enhanced synergic properties [34]. The core–shell structure of CNT-PANI is expected to be formed via the strong $\pi-\pi$ conjugation of the quinoid rings of PANI and the benzenoid rings of CNTs. On the other hand, the CNT core structure has a significant influence on the properties of the final composite such as charge-transfer, catalytic activity, and bulk conductivity. Few-walled CNTs (FWCNTs) have been recently proposed as an intermediate between single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs), displaying the appropriate combination of structural perfection and remarkable electronic properties [35]. Most importantly in this context, only layers accessible to the electrolyte will contribute to the electrochemical activity. While the conductivity of N-SWCNTs is dramatically lowered by doping due to the perturbation of the quasi-1D channel of the tubes by the charged dopants [6,36], using FWCNTs minimizes the volume and mass of the inactive inner layers but still retains the required good conductivity.

In this work, high quality FWCNTs of 2–5 walls were synthesized by chemical vapor deposition (CVD), carefully purified, functionalized and subsequently coated with PANI and carbonized at high temperatures. The obtained nitrogen-containing FWCNTs (N-FWCNTs) with only about 0.5 at.% nitrogen showed a remarkable high electrocatalytic activity toward ORR. Its high electrocatalytic activity examined both in an electrochemical cell and an alkaline methanol fuel cell. To the best of our knowledge, such a high electrocatalytic activity of N-CNT catalyst with this low nitrogen content has not been previously observed. The results of this work imply that other parameters than only the nitrogen content should be also considered for a good ORR electrocatalytic activity of N-CNTs, as discussed in Section 4.

2. Experimental

2.1. Catalyst preparation

FWCNTs were synthesized by catalytic pyrolysis of methane (CH_4) diluted with hydrogen (H_2) at 950 °C on cobalt–molybdenum (CoMo) oxides (5 at.%) supported on magnesium oxide (MgO) [37]. After synthesis, residual metal catalysts were removed by hydrochloric acid (HCl), rinsed properly with deionized water and dried in vacuum. In order to investigate the effect of pre-treatment

on the final doping level, a part of FWCNTs were subject to oxidative functionalization in 2 M HNO_3/1 M H_2SO_4 (1:1) solution under reflux conditions at 120 °C for 4 h. PANI was deposited both on the functionalized and the merely purified FWCNTs by the chemical oxidative polymerization of aniline monomers [38]. FWCNTs (0.5 g) were suspended in 1 M HCl (100 ml) and sonicated for a good dispersion. The aniline monomer (0.15 g) in 1 M HCl was added dropwise into the suspension and stirred for 1 h. The oxidizing agent ammonium persulfate ((NH_4)$_2$$S_2$$O_8$, APS) was dissolved in 1 M HCl and added dropwise (1:1 mass ratio of APS to aniline) under constant vigorous stirring in an ice bath (at 0 °C). The mixture was stirred for 6 h to achieve a good degree of polymerization. Finally, the reaction was terminated by the addition of acetone. The resulting products were filtered, washed with deionized water, and dried in vacuum. Then PANI-FWCNTs composites were pyrolyzed for 1 h at 600 °C and 900 °C in an argon flow to obtain N-FWCNTs. The samples are coded as follows: FW-Pr for the merely purified FWCNTs, FW-F for the functionalized FWCNTs, NFW-Pr-900 for the N-FWCNTs pyrolyzed at 900 °C using purified FWCNTs, and NFW-F-600 and NFW-F-900 for the N-FWCNTs pyrolyzed at 600 and 900 °C, respectively using the functionalized FWCNTs.

2.2. Physical characterizations

Scanning electron microscopy (SEM) was carried out with a JEOL field emission microscope JSM-7500FA equipped with an energy dispersive X-rays spectrometer (EDXS). High resolution transmission electron microscopy (HR-TEM) was conducted with a JEOL double Cs-corrected TEM (JEM-2200FS) operated at an acceleration voltage of 200 kV. Raman analysis was performed using a Horiba LabRAM HR spectrometer equipped with a CCD camera and a 633 nm excitation laser. X-ray photoelectron spectroscopy (XPS) was carried out with a Surface Science Instruments SSX-100 ESCA spectrometer using monochromatic AlK$_\alpha$ X-rays and an electrostatic hemispherical analyzer. The spectra were recorded with pass energy of 100 eV and an X-ray spot size of 600 μm.

2.3. Electrochemical characterizations

Glassy carbon electrodes (GCE, 0.196 cm^2) were polished and dried. The working electrode was prepared as follows: 5 mg of the catalyst powder, 476 μl of ethanol, and 24 μl of FAA3 anion exchange ionomer (solution of 12 wt.% FAA3 in N-methyl-2-pyrrolidone (NMP), supplied by Fuma-Tech) were mixed for 2 h and sonicated to form a uniform catalyst ink. Then a 7 μl drop of ink was carefully deposited on the GCE. The electrochemical characterization was performed in a conventional three-electrode cell comprising the modified GCE as working electrode, Pt wire as counter electrode, and Ag/AgCl/3 M KCl as the reference electrode (RE) using an Autolab PGSTAT12 potentiostat controlled by the GPES software. All potentials reported in this study were referenced to that of the Ag/AgCl electrode. The ORR measurements were carried out in an O$_2$ saturated 0.1 M KOH solution at room temperature. Cyclic voltammetry (CV) experiments were carried out in a potential range from 0.2 to −1.2 V at 10 mV s^{-1} scan rate. In order to evaluate the reproducibility of the electrochemical measurements three electrodes were prepared with each catalyst sample and the relative standard deviation (R.S.D.) of the peak current density was around 5%. The batch-to-batch repeatability was slightly lower, with a R.S.D. of 8–10%. Rotating disk electrode (RDE) measurements were performed at 5 mV s^{-1} scan rate and different rotation speeds (ω) from 100 to 3600 rpm. Rotating-ring disk electrode (RRDE) experiments were performed using the RRDE setup from Pine Research Instrumentation. The disk potential was scanned at 5 mV s^{-1} while the Pt ring electrode potential was fixed at 0.5 V. The