Journal of Power Sources 269 (2014) 54–60

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Lysine-derived mesoporous carbon nanotubes as a proficient non-precious catalyst for oxygen reduction reaction

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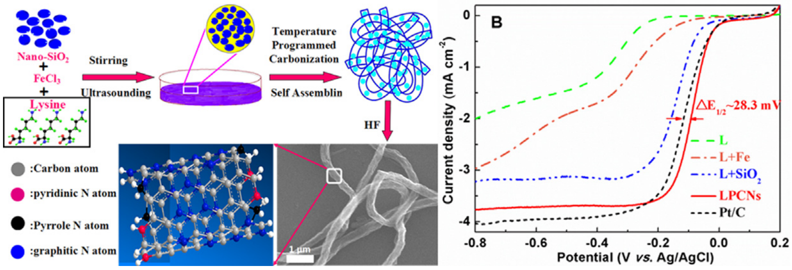
HIGHLIGHTS

- Porous carbon nanotubes with a diameter of ca. 300–400 nm (LPCNs) derived from lysine.
- LPCNs exhibit higher activity than Pt/C (20 wt%) for oxygen reduction reaction (ORR).
- LPCNs show higher stability for ORR and tolerance for methanol than Pt/C (20 wt%).
- The superior performance of LPCNs results from the unique structure and the doped effect.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 March 2014
Received in revised form
27 June 2014
Accepted 27 June 2014
Available online 7 July 2014

Keywords:
Oxygen reduction reaction
Catalyst
Carbon nanotube
N-doped
Mesopore

ABSTRACT

N-doped carbon nanotubes are highly favored for use as electrocatalysts for oxygen reduction reaction (ORR) because of their relatively low cost and superior catalytic activity. Here, Lysine-derived porous carbon nanotubes (LPCNs) with large inner cavities of ca. 300–400 nm are reported as electrocatalyst for ORR. LPCNs exhibit 28.3 mV of more positive half-wave-potential than that of commercial Pt/C. In addition, LPCNs is much more stable and tolerant to fuel crossover effect than Pt/C. The above superiorities make it a promising candidate for substituting noble metal catalysts as a cathode catalyst for ORR.

1. Introduction

The cathodic oxygen reduction reaction (ORR) plays a crucial role in electrochemical energy conversion in fuel cells [1]. Pt-based materials have long been regarded as active catalysts for ORR [2]; however, these noble metal catalysts hinder to mass market fuel cells for commercial application due to their high cost, sluggish electron transfer kinetics, and limited supply [3]. Along with recent intensive research efforts in reducing or replacing Pt-based catalyst, a suitable substitute for Pt-based catalysts, nitrogen-doped carbon nanotubes were reported to exhibit excellent electrocatalytic performance for ORR [4]. Compared to commercially available Pt-based catalysts, these nitrogen-doped carbon nanotubes possess the advantages of low cost, excellent electrocatalytic activity, free from CO poisoning, fuel crossover effect and long durability [5]. The

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http://dx.doi.org/10.1016/j.jpowsour.2014.06.156

enhanced electrochemical performance of nitrogen-doped carbon nanotubes toward ORR could be attributed to two sides; one is the well-defined high surface area which introduces spacing for improved electrokinetics, as well as good electrical and mechanical properties. Another is the electro-accepting ability of nitrogen species, which creates net positive charges on adjacent carbon atoms to facilitate oxygen adsorption for ORR with low overpotential [6].

The approach for the synthesis of nitrogen-doped nanotubes commonly used is chemical vapor deposition (CVD) [4,6,7], which employs liquid organic molecules as a carbon source to synthesize nanotubes on the base material via rearranging the carbon and nitrogen atoms on the metal catalysts at high temperatures [8,9]. In this case, the drawbacks are the use of expensive precursors and rigorous conditions or special instruments required [10]. In addition, some nitrogen precursors, such as NH_3 [11] used in the CVD process, are toxic, and careful treatments are essential, which may limit the practical application of these gas-phase synthesis methods. Therefore, creating nitrogen-doped nanotubes catalysts entirely derived from abundant, non-toxic precursors by a facile approach are of great importance for fuel cells.

On the other hand, a nanoporous structure with large surface area is highly desirable for electrochemical activity of these promising nanotubes. Efforts to construct nanoporous structure along with large surface area usually involve the templating approaches. Yang et al. prepared mesoporous nitrogen-doped carbon materials with high surface areas up to 1500 $m^2\ g^{-1}$ by using SiO_2 nanoparticles as hard templates [12]. A three-dimensionally ordered macroporous graphitic C_3N_4/carbon composite was fabricated by using SiO_2 nanoparticles for mesostructure control [13]. In our previous work [14], lysine-derived nitrogen-doped porous nanotubes (LPCNs) using SiO_2 nanoparticles as the template were prepared, which have rugged wall and much larger diameter than other reports, thus, have large specific surface area. In this work, the resultant LPCNs were demonstrated to show superior electrocatalytic activities compared to commercial Pt/C due to the formation of the unique architecture and synergic effect from Fe and N.

2. Experimental

2.1. Chemicals and materials

Lysine (Lys) was purchased from Shanghai Kangda Amino Acid Factory. Silicon dioxide (SiO_2, ca. 30 ± 15 nm) was purchased from Aladdin. Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) was purchased from Yantai Shuangshuang Chemical Co., Ltd. All chemical reagents used in this experiment were of analytical grade and used without further purification. Deionized water was used in all of experiment ($\geq$18 MΩ).

2.2. Preparation of lysine-derived porous carbon nanotubes (LPCNs)

To prepare LPCNs, 2 g lysine were dissolved into $FeCl_3$ methanol/water solution ($V_{methanol}$:V_{water} = 2:1) with stirring magnetically. Subsequently, the mixed solution was ultrasonicated for 1 h at room temperature. Then, 426 mg SiO_2 nanoparticles were added to the mixture under ambient conditions stirred and ultrasonicated for 2 h to obtain a homogeneous mixture and was dried at 80 °C in blast oven for overnight. The mass ratio of the lysine, $FeCl_3 \cdot 6H_2O$, and SiO_2 was about 20:4:1. The resulting powder of mixture were heated to 300 °C maintained for 1 h under nitrogen atmosphere in a tubular furnace. Then the mixtures was continuously heated under nitrogen flow at 5 °C min^{-1} to 900 °C and kept there for 1 h; and finally cooled down to room temperature. In order to remove SiO_2 template, the powders were treated according to the following SiO_2 template removal procedure: stirring of dispersion into HF (20 wt%, 6 mL) solution for 1 day with stirring magnetically at room temperature, washing 10 times with water, centrifugation to recover the powders. Finally, the products were dried at 60 °C overnight to obtaine LPCNs catalyst.

In order to study the effect of doped $FeCl_3 \cdot 6H_2O$, and SiO_2, carbon materials derived from lysine, lysine + $FeCl_3 \cdot 6H_2O$, and lysine + SiO_2, respectively, were prepared by the same process. The resultant products were denoted as L, L + Fe, and L + SiO_2, respectively.

2.3. Characterization

TG-DSC was performed with a TG/DSC-1 instrument system (Mettler Toledo, Swiss). Samples were put in a 70 μL aluminium crucible with a programmed heating rate of 10 °C min^{-1} from room temperature to 1000 °C under nitrogen atmosphere. Element analysis was performed by an Organic Elemental Analyzer, Thermo Flash 2000. XPS was obtained by a VGEscalab210 spectrometer fitted with Mg 300 W X-ray source (England). Scanning electron microscope (SEM) measurements were carried out on a Carl Zeiss Ultra Plus (Germany). Transmission electron microscopy (TEM) measurements were carried out on a JEM-2010 Electron Microscope (Japan) with the acceleration voltage of 200 kV. Raman spectroscopy measurements were carried out on a Ft-Raman spectroscopy (RFS 100, BRU-KER) employing Nd: YAG laser wavelength of 1064 nm. The sorption isotherm was carried out on Quantachrome Autosorb-1 volumetric analyzer.

2.4. Electrochemical measurements

The electrochemical measurement was evaluated on an electrochemical work station (CHI650). A conventional constant temperature three-electrode cell was used, including an Ag/AgCl (saturated KCl solution) electrode as the reference electrode, a platinum wire as the counter electrode, and Rotating disk electrode (RDE, 5 mm in diameter, 0.196 cm^2) as the working electrode. The thin-film electrode was prepared as follows: 5 mg of catalyst was dispersed ultrasonically in 1 mL Nafion/ethanol (0.25% Nafion) for 5 min. 8 μL suspensions dropped on the surface of the glassy carbon rotating disk electrode, followed by drying in air at room temperature. The loading of catalysts is ca. 20.4 mg cm^{-2}. Before each measurement, the electrolyte, 0.1 mol L^{-1} KOH solution, was purged with high-purity N_2 or O_2 gas for at least 15 min to ensure the gas saturated. All test temperature was controlled to 30 °C.

3. Results and discussion

As shown in Scheme 1, the synthesis of LPCNs involves a programmed thermal reaction to yield SiO_2 nanoparticles inserted Fe, N-doped carbon nanotubes, and then HF acid leaching of SiO_2 nanoparticles and soluble Fe species. The chemical reaction during pyrolysis of the lysine, SiO_2, and $FeCl_3 \cdot 6H_2O$ composite was studied by thermogravimetric-differential scanning calorimetry analysis (TG-DSC) analysis, which is shown as Figure S1 (Supporting Information). From the data, it can be observed that the formation of LPCNs involves two steps, e.g. decomposition and self-assembly processes, as shown in Scheme 1.

The morphology of LPCNs was observed by scanning electron microscope (SEM) and transmission electron microscopy (TEM) techniques (Fig. 1). As can be seen from Fig. 1A, LPCNs exhibit the morphology of open-ended, curved tube with the additional presence of some carbon debris. However, a few bright points are