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High stability of oxidation of methanol catalyzed by Pt supported by oxygen-incorporated bamboo-shaped CNTs grown directly on carbon cloth

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ABSTRACT

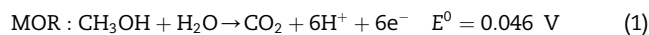
Bamboo-shaped CNTs in which oxygen was incorporated were directly grown on carbon cloth (O-BCNT-CC) by microwave plasma-enhanced chemical vapor deposition. Mixed precursors CH₄/H₂/N₂/O₂ were introduced during the growth process. For comparison, bamboo-shaped CNTs without incorporated oxygen were prepared herein (BCNT-CC). Then, platinum catalysts were prepared on the as-grown O-BCNT-CC (Pt/O-BCNT-CC) and the as-grown BCNT-CC (Pt/BCNT-CC). According to TEM-EELS oxygen mapping, O atoms were uniformly distributed on the O-BCNT surface. Methanol oxidation was performed using Pt/O-BCNT-CC and Pt/BCNT-CC in 1 M methanol and 1 M sulfuric acid by cyclic voltammetry. In the initial cycle, the peak current density of Pt/O-BCNT-CC was almost equal to that of Pt/BCNT, indicating that both had nearly equal activities in the beginning. After 300 cycles, the peak current of Pt/BCNT-CC was reduced to half of the initial peak current owing to platinum-poisoning; however, the peak current of Pt/O-BCNT-CC decayed less. In Pt/O-BCNT-CC, the oxygen-containing functional groups affect the orientation index of crystalline Pt, providing a means of oxidizing methanol and stabilizing Pt catalysts for the long-term.

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1. Introduction

A direct methanol fuel cell (DMFC) is an electrochemical power generator that uses methanol as a fuel at the anode and air/oxygen at the cathode. A DMFC uses liquid methanol below 70 °C, and requires no humidifier or reformer. It is therefore regarded as a promising power source for portable applications. In the overall redox reaction, the methanol

oxidation reaction (MOR) is thought to be a slower step than the reduction of oxygen at the anode,

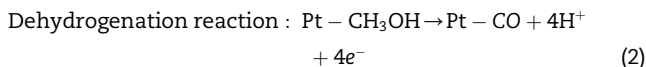


Pt-based catalysts, which are relatively stable and reactive in the acid environment of the DMFC, are utilized to accelerate the MOR. Previous studies of the MOR over Pt [1,2] show that MOR involves a series of dehydrogenations, in which the

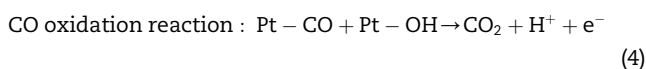
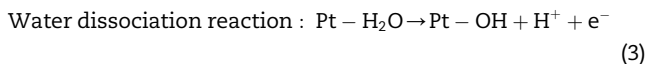
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sequential stripping of protons and electrons is believed to take place, resulting in the formation of carbon-containing intermediates,



In this step, the surface of Pt is thoroughly covered by $-\text{CO}_{\text{ads}}$; this process is called “Pt-poisoning”, and slows down the reaction. $\text{Pt}-\text{CO}_{\text{ads}}$ is detoxified by a water dissociation reaction in the formation of the $-\text{OH}_{\text{ads}}$ species (reaction (3)), which reacts with $-\text{CO}_{\text{ads}}$ by the Langmuir–Hinshelwood mechanism to form CO_2 (reaction (4)).



The water dissociation reaction on Pt occurs at high potential (>0.6 V) at the anode, and is not efficient at the anode. Accordingly, binary Pt-based catalysts (such as Pt–Ru, Pt–Ir and Pt–W) have been reviewed, which provide $-\text{OH}_{\text{ads}}$ by the dissociation of reaction of water at low potential [3,4]. Among binary Pt-based catalysts, the Pt–Ru catalyst is the most active, and its high MOR activity is attributed to a bi-functional mechanism [5] and a ligand effect [6].

Recently, the development of DMFC has focused on improving catalytic activity and reducing cost. Accordingly, various works have demonstrated nanoscale catalysts that are supported by carbon nanotubes (CNTs), carbon nanofibers and graphene [7–12]. To obtain uniformly dispersed catalysts on CNT surfaces, the distribution of functional groups on the surface of CNTs, which serve as nucleation sites, is essential. Since a CNT is a graphene sheet that is rolled into a cylinder with a diameter of the order of a nanometer, the aromatic rings of CNT-sidewalls must be disrupted to improve the adhesion of the catalyst. Usually, CNTs are oxidized by HNO_3 , H_2-O_2 , ozone, oxygen plasma and microwave assisted synthesis to create oxygen-containing functional groups (OFGs), such as carboxyl ($-\text{COOH}$), carbonyl ($-\text{CO}$), and hydroxyl ($-\text{OH}$) [13–17]. As a result, these OFGs stabilize the CNTs in water or any other polar solvent by developing negative surface-charges and promoting the dispersion of the CNTs via mutual electrostatic repulsion. Although strong oxidation is useful for forming OFGs on the surface of CNTs, some studies have demonstrated that various functionalization methods have a direct impact on the intrinsic properties of CNTs, which include electrical resistance, adsorption and wettability [18–23]; these characteristics have been proven strongly to affect the dispersion, loading and activity of catalysts that are supported by functionalized CNTs [22–26]. Larsen and Skou have investigated the effects of various surface-functionalized CNTs on catalytic activity, which hydroxyl-functionalized graphitized CNTs with high oxygen content demonstrated a remarkably high activity in their studies [24]. Most of the many studies on the formation of OFGs on the surface of CNTs have involved functionalization after the synthesis of CNTs. Hence, a new functionalization method for use during CNT synthesis that can simply and

effectively functionalize the surface of CNTs to create uniform OFGs must be developed. Some investigations have demonstrated nitrogen-doped CNTs as catalyst supports, in which graphene sheets are doped with nitrogen atoms to promote the formation of bamboo-shaped CNTs (BCNTs) [27–29]. When Pt-based catalysts are supported by BCNTs, the substituted nitrogen sites may be the initial nucleation sites of the deposition of catalytic nanoparticles, not only improving the dispersion of the catalytic nanoparticles but also increasing catalytic activity. In our earlier studies, Pt-based catalysts that were supported by CNTs that were directly grown on carbon cloth have performed very well in DMFC and PEMFC applications, owing to rapid electron transfer associated with the direct growth of the CNTs and their direct delivery to the carbon cloth, reducing the energy loss during the electron transport [30–33].

In this work, the bamboo-shaped CNTs with incorporated oxygen were directly grown on carbon cloth (O-BCNT-CC). During the synthesis, oxygen-containing precursors were introduced, and OFGs were uniformly formed on the O-BCNT surface. Subsequently, Pt catalysts were uniformly deposited on the oxygen-incorporated BCNTs (Pt/O-BCNT-CC). This work establishes that Pt/O-BCNT-CC has not only high activity but also high stability in the MOR.

2. Experimental

O-BCNT-CC was prepared by iron-assisted catalyzed growth in a microwave plasma-enhanced chemical vapor deposition (MPECVD) reactor. The iron was sputtered on the carbon cloth using an ion beam sputtering deposition system (Commonwealth Scientific. Co., Ltd.). The carbon cloth was positioned in parallel with the iron target (99.95%), 20 cm away from it, while an ion beam was incident at 40° onto the target from a Kaufman type ion source. During the deposition, the Kaufman ion source was operated at a beam voltage and current of 1250 V and 20 mA, respectively, for 10 min in an atmosphere of argon at a pressure of 5×10^{-4} Torr. Subsequently, iron-coated carbon cloth was introduced to the MPECVD reactor. O-BCNT-CC was synthesized in the mixed precursors $\text{CH}_4/\text{H}_2/\text{N}_2/\text{O}_2$ with CH_4 , H_2 and N_2 flow rates fixed at 20, 80 and 80 sccm, respectively. O_2 flow rates of 0.2, 0.8 or 1.5 sccm, were employed to investigate the effects of this rate on the O-BCNT-CC. The O-BCNT-CC thus formed was denoted O-BCNT-CC(0.2), O-BCNT-CC(0.8) and O-BCNT-CC(1.5), respectively. The growth condition was a microwave power of 1.5 kW, a chamber pressure of 40 Torr, and a substrate temperature of 900°C for 10 min. In this work, when oxygen was fed at a high flow rate of above 2 sccm, into the reactor, the plasma was not stable and could not stably maintain the growth. For comparison, BCNT-CC without incorporated oxygen was also prepared. To obtain Raman spectra and X-ray photoelectron spectra of BCNTs without the background associated with the carbon cloth, BCNTs were directly grown on the Si substrates under the same conditions, and denoted O-BCNT-Si(0.2), O-BCNT-Si(0.8) and O-BCNT-Si(1.5).

To prepare Pt/O-BCNT-CC and Pt/BCNT-CC, platinum nanoparticles were deposited on the substrates using a sputtering system. The deposition proceeded in an argon atmosphere with a working pressure of 5×10^{-2} Torr at room

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