INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–8

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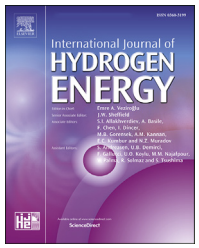

Effect of methane concentration on oxygen reduction reaction of carbon films in alkaline solution

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ARTICLE INFO

Article history:
Received 25 January 2018
Received in revised form
19 July 2018
Accepted 1 August 2018
Available online xxx

Keywords:
Carbon film
Fuel cells
Oxygen reduction reaction
Electrocatalyst

ABSTRACT

Carbon films have been prepared by the hot filament chemical vapor deposition method at different methane concentrations. The morphology, microstructure, and chemical bonding states of the deposited films were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). The electrocatalytic oxygen reduction reaction (ORR) activity of these carbon catalysts in alkaline solution was investigated using rotating disk electrode (RDE) voltammetry. The experimental results show that the sp^2/sp^3 value increases with increasing methane concentration (MC), while the I_D/I_G value (integral area ratio of D and G band) gradually becomes larger and reaches the maximum at a MC of 3%, then decreases. With an increase in the MC, the ORR peak potential successively shifts to a more positive value and remains a constant at the MC of 3.5%. The peak current density consecutively increases to a summit at the MC of 3% and then begins to decrease. The onset potential shifts positively and the limiting diffusion current density at −1.0 V increases gradually, indicating that the catalytic activity towards ORR of the catalysts is progressively enhanced. When the MC is more than 3%, the catalytic activity begins to decay. Moreover, the catalysts with a better ORR activity have a poorer durability and methanol tolerance.

Introduction

The oxygen reduction reaction (ORR) on the cathodes is one of the important factors to determine the performance of fuel cells. Generally, there are two different paths for the ORR, namely, the two-electron process of HO_2^- as an intermediate product and the more efficient four-electron pathway of H_2O. The rate of the ORR is decided by the catalytic activity of cathode materials. The energy conversion efficiency will be observably reduced if the reaction rate is too slow [1,2]. Although commercial Pt/C catalyst can efficiently catalyze oxygen, there are still some serious problems including instability and poor methanol tolerance. In addition, high price and shortage of the Pt raw material also hamper the large-scale commercialization of the fuel cells [3,4]. It is

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https://doi.org/10.1016/j.ijhydene.2018.08.004

therefore very necessary to develop new catalysts with efficiency, stability, good methanol tolerance, and low cost.

All these years, heteroatoms (B, N, P and S [5–8] etc.) doped carbon-based catalysts (graphite, graphene, carbon nanotubes, mesoporous carbon, and diamond [5,6,9–11] etc.) as substitutes for the platinum-based materials have been devoted much attention. Due to generating a very large amount of heat in operation of the fuel cells, the catalytic materials with a higher thermal conductivity are urgently needed for the sake of promoting working efficiency of the fuel cells. In this case, diamond with a much higher thermal conductivity (2000 W/(m·K)) than that of graphite (129 W/(m·K)) is more suitable for the catalytic material. In our previous works, it indicated that graphitized porous diamond by doping boron also displayed a superior oxygen reduction activity. The result was in agreement with the report by Macpherson et al. [12], in which the ORR peak was observed on the BDD with sp^2 carbon surface and as comparison the BDD with sp^3 diamond surface not had the ORR performance. The effective transference of electrons depends on the catalytic sites on the catalyst surface, and hence the surface of BDD with sp^3 structure is catalytically inert. The lack of "binding sites" cannot promote electron transference between the surfaces of the catalytic materials and the reactant gas molecules. Oxygen therefore cannot be reduced on the electrode surface. The ORR is possible when the sp^2 phase is present. It is well known that the four valence electrons form four highly stable σ bonds for sp^3 hybrid orbitals, while the three valence electrons form three σ bonds for sp^2 hybrid orbitals, and the fourth valence electron forms a weak π bond. The intrinsic carbon defects can activate the π electrons of sp^2 carbon to generate oxygen reduction activity [13]. The aforementioned fact indicates that the sp^2-bonded carbon also plays an important role on the catalytic activity of the oxygen reduction [14,15]. Obviously, it is very necessary to investigate the influence of the sp^2 content on the ORR performances in order to maximize catalytic potential of the carbon catalysts.

In this paper, carbon films are fabricated on titanium substrates using different methane concentrations (MCs) by a conventional hot filament chemical vapor deposition (HFCVD) technique. The effect of the methane concentration (MC) on the ORR activity is studied by estimating the potential and the current density of the oxygen reduction peak, together with the onset potential and the limiting diffusion current density. Durability and methanol tolerance are also evaluated.

Experimental

Material synthesis

Carbon films were prepared utilizing a HFCVD technique. Pure titanium piece with 15 mm in diameter and 1 mm in thickness was used as substrate. All the substrates were polished using diamond paste and ultrasonically cleaned in acetone, ethanol and deionized water for 10, 10 and 5 min successively, and then dried in air. The pretreated titanium sheet was put on the sample stage in the reaction chamber. The distance between the tantalum filament and the substrate was approximately 5–8 mm. The volume proportion of CH_4 to H_2 was fixed at 1%, 1.5%, 2%, 2.5%, 3%, and 3.5%. The chamber pressure was kept at a total pressure of 3 kPa and the films were deposited for 6 h at a substrate temperature of about 1100 K.

Physical characterizations

The morphologies of the deposited films were observed by means of scanning electron microscopy (SEM, Zeiss Supra55) and transmission electron microscopy (TEM, Tecnai G220 S-Twin). X-ray diffraction (XRD, PANalytical B.V. Empyrean) with Cu $K\alpha$ ($\lambda = 0.154$ nm) radiation at a voltage of 30 kV was used to characterize the phase structure. The chemical composition and the carbon bonding state were characterized by X-ray photoelectron spectroscopy (XPS) with an ESCALAB 250Xi spectrometer using a focused and monochromatized Al $K\alpha$ radiation ($h\nu = 1486.6$ eV). Raman spectra were collected on a Raman spectrometer from Renishaw Co. (Renishaw inVia, He–Ne laser excitation of wavelength 633 nm) to analyze the structure and the quality of carbon materials.

Electrochemical characterizations

Free-standing carbon films were obtained by etching the titanium substrates with 5 wt% HF acid to study the ORR catalytic properties. The exfoliated carbon pieces were dispersed in a mixed solution of deionized water and isopropanol at a volume ratio of 3:1 to form a suspension with a concentration of 5 g L^{-1}. Afterwards, 10 μL suspension was dropped onto the glassy carbon electrode (GCE) and then covered with 3 μL Nafion solution (0.5 wt%) as a binder. A three-electrode system (Shanghai Chen Hua, CHI760E) and a rotating disk electrode (RDE, ALS Co., Ltd. RRDE-3A) with GCE (3 mm in diameter) were used in the measurements. The current density was evaluated with respect to the geometrical cross-sectional area (0.07065 cm^2) of the supporting GCE disk. Electrochemical impedance spectroscopy (EIS) was performed in a frequency range from 0.01 Hz to 100 kHz with an amplitude of 5 mV. Catalytic activity of the samples was evaluated from the cyclic voltammetry (CV) and the linear sweep voltammetry (LSV) experiments. The CV measurements were carried out in N_2– (as a comparison experiment) and O_2-saturated 0.1 M aqueous KOH solution at a scanning rate of 50 mV s^{-1}. The LSV tests were conducted at different rotation rates from 200 to 2600 rpm in O_2-saturated 0.1 M aqueous KOH electrolyte at a scanning rate of 5 mV s^{-1}. The durability and methanol tolerance tests were conducted in O_2-saturated 0.1 M aqueous KOH solution using a chronoamperometry at room temperature.

Results and discussions

The surface morphologies of the samples were observed by SEM and TEM. Fig. 1 shows the SEM images of the deposited carbon films at various MCs ranging from 1% to 3.5%. With the increase of methane concentration, the grain sizes diminish gradually and the film surface becomes smoother. The film exhibits well-faceted characteristic when the volume proportion of CH_4 to H_2 is in the range from 1% to 1.5%, as shown in Fig. 1a and b. With further increase in methane

Please cite this article in press as: Suo N, et al., Effect of methane concentration on oxygen reduction reaction of carbon films in alkaline solution, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.08.004