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Highly sensitive amperometric Nafion-based CO sensor using Pt/C electrodes with different kinds of carbon materials

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ABSTRACT

In this paper, a novel amperometric CO sensor using Nafion and Pt/C composite electrodes was fabricated. Three kinds of carbon materials (carbon fibers, multiwall carbon nanotubes and carbon blacks) were utilized as the supports of the sensing and reference electrodes for the CO sensors. The results revealed that the effective Pt loadings on the electrodes increased in the following order: carbon fibers (CFs) > multiwall carbon nanotubes (MWCNTs) > carbon blacks (CBs), leading to the increasing of the sensitivities toward CO in same order. In other words, the sensor using Pt/CFs as the sensing electrode (SE) showed the highest sensitivity with the value of 0.077 μA/ppm and shortest response time in the range of CO concentration from 1 to 200 ppm at room temperature. Further, a reproducible and stable response against 50 ppm CO was obtained for the sensor with Pt/CFs SE materials. Moreover, a low detection limit of 0.1 ppm for CO was also examined, suggesting that the sensor can be convenient for detecting very low traces of CO.

1. Introduction

Recently various kinds of gas sensors are required for monitoring carbon monoxide (CO) from the combustion exhaust such as automobiles, industrial plants and gas stoves, because CO is inflammable and can cause great harm to the body by bonding tightly with the hemoglobin, preventing the combination to oxygen [1–3]. Commonly, there are three types of sensors: semiconductor sensors based on SnO_2 [4–6], In_2O_3 [7,8], and so on, catalytic combustion sensors [9] and electrochemical sensors which are operated either in amperometric [10–12] or potentiometric mode [13–15].

Among the amperometric type electrochemical sensors, the gas sensor employing the Nafion membrane as the solid electrolyte, which shows good mechanical, outstanding chemical stability and excellent conductivities under the condition of high water vapor, has drawn more and more attentions recently [16–18]. Moreover, this type of sensors always works at room temperature and the response signals are almost proportional with the gas concentrations. For these sensors, the catalyst materials deposited on the Nafion membrane are indispensable for the gas detection. For example, K.C. Ho [19] has reported a NO gas sensor based on Pt/Nafion electrodes at a concentration of 500 ppm. Beyond that, the binary Pt-Ru electrode materials have also been prepared to detect H_2 by Y.C. Weng et al. [20]. Now it is well known that the addition of noble metals is an effective strategy to enhance sensing performance to target [21,22]. Nevertheless, the use of noble metals also has some drawbacks such as the self-aggregation of metal particles which may decrease the active surface areas for the interactions between gases and catalyst powders, expensive cost and poor selectivity.

A large number of ways have been adopted to overcome the above shortcomings. One of promising solution proposed for improvement is to deposit the metal nanoparticles (NPs) on some supports. Among them, alternative carbon materials like carbon blacks [23], ordered mesoporous carbons [24], carbon nanotubes [25–27] and carbon nanofibers [28–31] have been successfully prepared to support the metal NPs for applications in electrochemical catalysis and fuel cells because of their excellent conductivity and porous microstructure for dispersion of metal particles and gas transformation. Herein, a great deal of attentions have been drawn on the kinds of carbon supports for the homogeneous deposition of Pt NPs due to their unique surface structures, excellent mechan-

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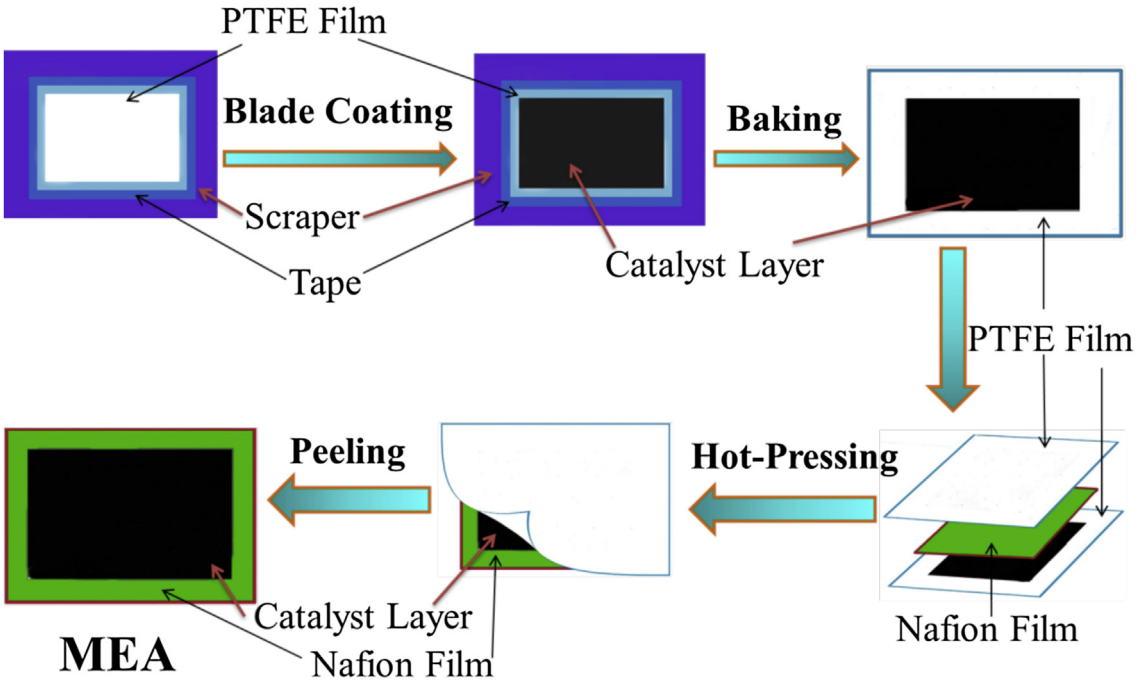

Fig. 1. Fabrication of the membrane electrode assembly (MEA) for the sensor.

ical properties, high electric conductivity and large surface areas [32,33]. For instance, Y.C. Liu et al. [34] have prepared a solid state H_2 sensor using Pt particles supported on activated carbon powders by the indirect wetting method and found that the sensitivity is 0.716 μA/ ppm at a Pt loading of 3.0 mg/cm^2. Besides, B. Zhao et al. [31] have employed the incipient wetness impregnation and electrodeposition methods to prepare a novel electrocatalyst, Pt NPs supported on activated carbon fibers, for the electrocatalytic hydrogenation of furfural to furfuryl alcohol. As far as we know, however, very few researchers have developed CO sensors by fabricating the sensing electrodes with noble metal particles supported on these carbon materials.

In this work, the Pt NPs deposited on CBs, MWCNTs and CFs, respectively, are utilized as the composite SE materials for the Nafion-based CO sensor. The differences of the microstructure for three types of catalytic powders have been discussed. Besides, when fabricating the amperometric sensor based on Nafion membrane, it is particularly critical to attain an excellent contact between Nafion membrane and catalytic materials for good proton and electronic conductivity. An effective way for obtaining the excellent contact is the hot-pressing method. After hot-pressing, the varieties of Nafion membranes attached with three kinds of catalytic materials (Pt/CBs, Pt/MWCNTs and Pt/CFs) have been obtained. Beyond that, the sensing properties and mechanism of the Nafion-based amperometric CO sensor have been investigated.

2. Experimental

2.1. Preparation of Pt NPs with different carbon supports

The Pt NPs are reduced from hexachloroplatinic acid (H_2PtCl_6, Shanghai Wu Chemical Reagent Co., Ltd.) by using sodium borohydride ($NaBH_4$, Aladdin) as the reductant on three carbon supports: CBs (CABOT, U. S. A.), MWCNTs (XFNANO Co., Ltd.) and CFs (Beijingdaoking Co., Ltd.). The detailed procedure is as follows. First, the carbon support is suspended in deionized water with 50 mM H_2PtCl_6 solution and trisodium citrate ($Na_3C_6H_5O_7{\cdot}2H_2O$, Sinopharm Chemical Reagent Co., Ltd.) acted as the stabilizer at a carbon support/Pt/trisodium citrate weight ratio of 4:1:3 by ultrasonication for 30 min. Next, 50 mL $NaBH_4$ solution, which is obtained by dissolving the $NaBH_4$ powders into 50 mL 0.1 M NaOH solution to prevent the hydrolysis, is added into the resulting suspension dropwise with continuously magnetic stirring at 50 °C for 2 h. Then, such prepared Pt/C powders are cleaned with deionized water and dried at 80 °C for 12 h.

2.2. Fabrication and measurement of the amperometric CO sensor

The amperometric CO sensor is fabricated using the fuel cell prototype as described in our previous work [35]. The prototype contains a membrane electrode assembly (MEA) composed of two catalyst layers hot pressed at 90 °C and 8 MPa on a Nafion membrane which is pre-treated in 5% H_2O_2 solution, 0.5 M H_2SO_4 solution and deionized water at 80 °C, respectively. The MEA, which is inserted between the gas diffusion cap and isolation disc, is obtained by the scrapping method as shown in Fig. 1. 10 mg as-prepared Pt/C catalyst powders are well-distributed in 100 μL of pre-arranged dispersant which includes 100 μL 5 wt.% Nafion solution used for attaining strong interactions between Nafion membrane and catalytic powders, 50 μL ethylene glycol (EG) and 200 μL deionized water on polytetrafluoro-ethylene (PTFE) film. Then two pieces of resulting films are dried at 90 °C and hot-pressed with the Nafion membrane. Finally, the PTFE films are peeled away and the MEA is immersed in deionized water for 12 h. Three kinds of MEAs containing Pt NPs supported on CBs, MWCNTs and CFs are labeled as M_a, M_b and M_c, respectively. Correspondingly, CO sensors fabricated by above three types of MEAs are defined as S_a, S_b and S_c, respectively. Based on the remaining volume of catalyst inks on the surface of PTFE films after hot-pressing, the Pt loadings of