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Effect of the dispersants on the performance of fuel cell type CO sensor with Pt–C/Nafion electrodes

Yehui Guan, Mingjun Dai, Tong Liu, Yingwei Liu, Fangmeng Liu, Xishuang Liang*, Hui Suo, Peng Sun, Geyu Lu*

State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, 2699 Qianjin Street, Changchun 130012, China

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ABSTRACT

A fuel-cell-type gas sensor based on the membrane electrode assemble (MEA) composed of proton exchange membrane (Nafion) and Pt/C sensing electrodes was fabricated for detection of CO at room temperature. The Pt/C electrodes materials were synthesized from Vulcan XC-72 carbon powders and hexachloroplatinic acid (H_2PtCl_6). This paper mainly focused on the effect of various dispersants (ethylene glycol (EG) tetraethyl orthosilicate (TEOS), glycerol and EG/polytetrafluoro-ethylene (PTFE)) on the performance of the presented sensor. Results revealed that the sensor utilizing EG as the dispersant elicited the highest response current toward 50 ppm CO. The current of the sensor was linearly correlated with CO concentration in the range of 1–200 ppm, which sensitivity was 88 nA/ppm. In addition, the 90% response and recovery times of the sensor toward 50 ppm CO were 22 and 24 s, respectively. Besides, the prepared CO sensor also had a good repeatability and acceptable selectivity.

1. Introduction

CO is a major atmospheric pollutant that can cause serious poisoning to the human body by binding tightly to hemoglobin in the blood and producing reductions in cellular respiration [1–3]. CO is commonly generated by incomplete combustion of fuel in vehicles. Thus the monitoring of toxic CO has gained increasing attention from governments and researchers.

Different kinds of chemical sensors for CO detection have been developed, including conductive-type sensors that use the semiconductor oxides, catalytic combustion-type sensors, electrochemical-type sensors and solid electrolyte-type sensors [4–6]. Among these sensors, semiconductor oxide-type sensors using the metal oxides such as SnO_2 [7–9], ZnO [10–12], Zn_2SnO_4 [13] and $LaCoO_3$ [14] have been widely investigated in recent years because of their low cost and simple fabrication process. For example, Wurzinger and Reinhardt [15] found that SnO_2 sensors doped with 2 wt.% Pt exhibit maximum sensitivity to CO at around 220 °C. However, semiconductor oxide-type sensors require to be heated to promote the redox reactions.

The catalytic combustion-type sensors detect CO gas via resistance changes resulting from the heat generated by the combustion of CO gas on Pt coil catalyst. Hosoya et al. [16] fabricated a catalytic combustion-type CO sensor that shows superior performance for CO detection at 60 °C with good selectivity by employing Pt-loaded CeO_2–ZrO_2–ZnO as the CO oxidizing catalyst. The catalytic combustion-type sensors also present the disadvantage of non-applicability in the absence of oxygen.

Electrochemical sensors operate at room temperature without a heater. These sensors often use H_2SO_4 and noble metals (Pt) as the liquid electrolyte and sensing electrode, respectively [17]. Thus they are usually rather bulky and easy to be dried. Moreover, they require good sealing to prevent electrolyte leakage.

Solid electrolyte-based CO sensors use yttria-stabilized zirconia (YSZ) [18–23] and NASICON ($Na_3Zr_2Si_2PO_{12}$) [24,25] as the electrolytes. This type of sensor exhibits good sensitivity and selectivity after optimization of the composition and microstructure of the gas-sensing electrodes as well as the electrolytes. Striker et al. [19] evaluated the effect of surface area on the performance of nanocomposite Au–YSZ electrodes and found that sensors with low-surface area Au electrodes were more sensitive to CO than nanostructured composite electrodes with large surface areas. Solid electrolyte sensors also present several drawbacks, such as complex fabrication processes and high working temperature.

Sensors based on proton exchange membranes (Nafion) have been developed for operation at low working temperature. Mochizuki et al. discussed the performance of fuel cell-type sensors using Nafion 117 membranes and found that the sensitivity

* Corresponding authors. Fax: +86 431 85167808.
E-mail addresses: liangxs@jlu.edu.cn (X. Liang), lugy@jlu.edu.cn (G. Lu).

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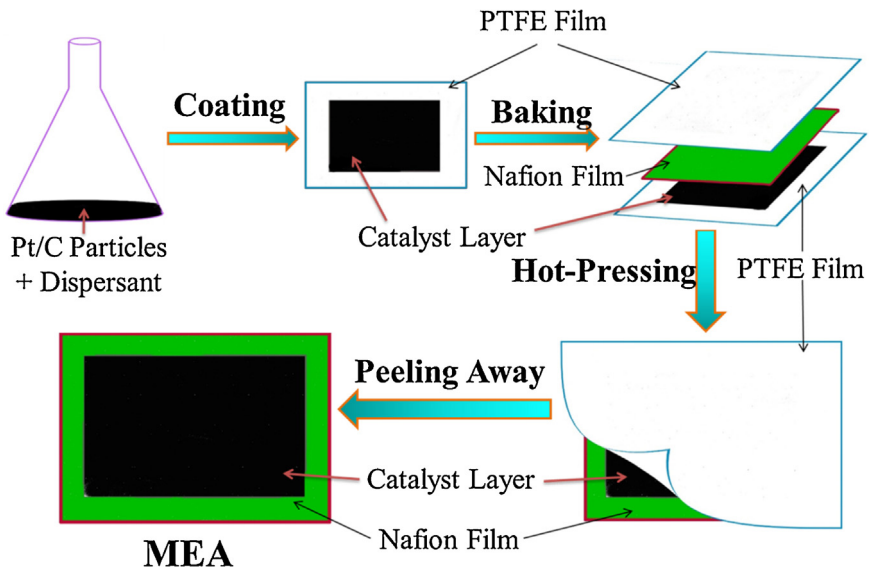

Fig. 1. Preparation protocol of the MEA.

of the sensors at low CO concentration was higher than that of combustion-type sensors [26,27]. These sensors are environment-friendly with excellent stability, accuracy and long lifetimes. They can operate at room temperature without any power consumption. Moreover, the sensor current shows a nearly linear relationship with CO concentration.

MEA, as an indispensable component of the Nafion-based electrochemical CO sensors, often features two structures: one is the thick-layer electrode, which is made up of the catalyst layer, diffusion layer and Nafion membrane; the other is called the thin-layer electrode, which contains the catalyst layer and Nafion membrane without a diffusion layer [28–30]. The Nafion membrane functions as the solid electrolyte to conduct the protons. The catalyst layer, containing Pt/C nanoparticles, is used for accomplishing the oxidation-reduction process. When combining the catalyst layer with Nafion film, three methods are applied: the Takenaka–Torikai (T–T) method, the impregnation–reduction (I–R) method and the hot–pressing (H–P) method.

When fabricated by H–P method, the Pt/C nanoparticles give rise to a physical boundary with the Nafion film. Thus, the dispersants are indispensable to closer contact between the Pt/C nanoparticles and Nafion film. The Pt/C nanoparticles can also be well dispersed in these solvents. Parts of the dispersants are volatilized during the hot-pressing process, resulting in large active surface area for redox reactions. Beyond that, the dispersants should be hydrophobic to make it easier for gas diffusion.

In this work, an excellent interface between the Nafion membrane and catalyst layers was fabricated using the solubilized Nafion solution. Two hydrophilic solvents (TEOS, EG) and two hydrophobic solvents (glycerol, PTFE) were used to disperse the Pt/C particles. The effects of four dispersants on microstructures and performance of the resulting sensors were determined.

2. Experimental

2.1. Preparation of the MEA

The CO sensor is fabricated using a thin-layer electrode, according to the method described by Wilson and Gottesfeld [30]. A typical preparation protocol is shown in Fig. 1. The catalyst inks are produced by mixing the Pt/C particles with 5 wt.% solubilized Nafion (DUPONT, U. S. A.), DI water and EG (TEOS, glycerol, EG/PTFE) at a

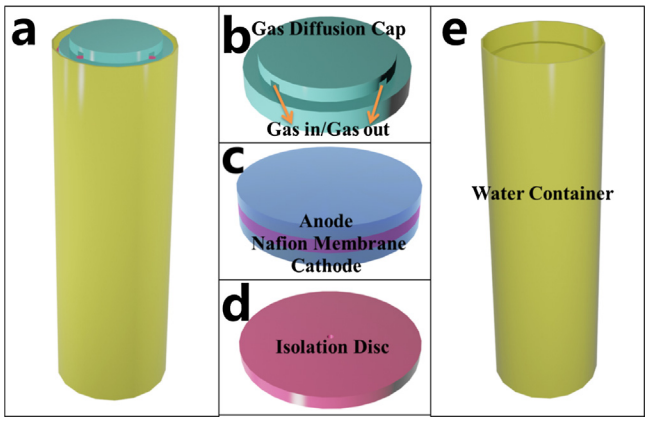

Fig. 2. Schematic of the fuel cell-type sensor (a), which is composed of (b) a gas diffusion cap, (c) the MEA, (d) an isolation disc and (e) a water container.

Pt–C/Nafion (dry)/water/EG weight ratio of 5:1:35:10 by a magnetic stirrer. The Pt/C particles is prepared from Vulcan XC-72 carbon powders (CABOT, U.S. A.) and H_2PtCl_6 (Shanghai Wu Chemical Reagent Co., Ltd.) solution with sodium borohydride ($NaBH_4$, Aladdin) as the reductant. After stirred, the catalyst inks are coated on two pieces of PTFE films (Shanghai Hesen Co., Ltd.) and baked in an oven at 80 °C until dry. Then the two PTFE films are combined with the Nafion membrane by H–P method at 125 °C and 8 MPa for 90 s. Prior to its use, the Nafion membrane is pretreated with 5% H_2O_2 (Beijing Chemical Works Co., Ltd.), 0.5 M H_2SO_4 (Beijing Chemical Works Co., Ltd.), DI water and 0.1 M NaOH for 1 h in sequence. Afterwards, the PTFE films are peeled from the Nafion membrane and the MEA is immersed in 0.5 M H_2SO_4 to regenerate H^+. MEAs using TEOS, EG, glycerol and EG/PTFE (Sinopharm Chemical Reagent Co., Ltd. and Aladdin) are defined as MEA (A), (B), (C) and (D), respectively.

2.2. Fabrication and measurement of the fuel cell type CO sensor

The sensor (Fig. 2a) consists of four components. The first component (Fig. 2b) is a cap filled with pieces of carbon cloth. Three evenly distributed holes on the surface of the cap act as the diffusion paths for CO gas. The second component (Fig. 2d) is a metal disc with a hole in the center, which can support the MEA for good