Scale like Co(OH)2/CoOOH modified platinum catalytic gas diffusion electrode and its application in ammonia detection

Hanpeng Dong*1, Zhengwei Wu1

1 State Key Laboratory of Transducer Technology, Aerospace Information Research Institute, Chinese Academy of Sciences, No. 19 North 4th Ring Road, Haidian District, Beijing, P.R. China

*donghp@aircas.ac.cn

Abstract. Platinum (Pt) is sputtered on porous PTFE membrane as the basic electrode. Cobalt hydroxide catalyst is deposited on the porous platinum/PTFE electrode by an electrochemical assisted deposition method with ammonia gas employed as precipitant. SEM image of the catalyst shows an integration of scale like flake of about 0.5 micrometer in diameter. The XRD analysis suggested that the catalyst is a mixture of β-Co(OH)2 and CoOOH. The mixture is regard as the effective constituent in the ammonia electrode reaction according to the electrochemical analysis. The cyclic voltammogram indicate that at higher than 0.4V (v.s. saturated HgO/Hg electrode reference) the catalytic activity of the working electrode increased significantly. With the modified electrode as working electrode and a pure platinum electrode as assistant electrode, a four electrodes sensor is established to measure ammonia in air successfully.

1. Introduction

Self-assembly of special catalytic materials on electrode has attract much attention for its application prospects in electrochemical devices such as fuel cells, chemical sensors, waste-water treatment plants. For example, platinum group metals have been reported as anode catalyst for electrochemical detection of ammonia. But these noble metals exhibited relatively low catalytic activities [1]. Co3O4 has been reported as an effective catalyst to ammonia oxidization. Its applications in high temperature solid-state electrochemical devices and automobile exhaust purifying system have been reported [2]. Co3+ is regard as the active species in the Co3O4 catalyst for ammonia oxidization reaction [3]. In another report, the existence of Co4+/Co3+ ion couple is regard as major reason of excellent catalytic activity of Co3O4 [4, 5, 6]. In summary, high-valance species of cobalt is much concern with the catalytic activeness to ammonia oxidization and is regard as the critical component in the catalyst. But the fundamental principle of the high catalytic activeness of the high-valence state cobalt to ammonia oxidization is still obscure.

The problems are raised when using Co3O4 as anode catalyst in gas diffusion electrode (GDE). First, most of the synthetic routes of Co3O4 involve a high temperature calcinations step at about 300°C [5, 7], which limit the using of some important organic materials such as polymers and paraffin in GDE. Second, the poor electric conductivity of Co3O4 at room temperature (about 104 Ω/cm) made it unsuitable for its application as high effective electrode material [6, 8].
In this study, an electrochemical assistant depositing method is developed to modify cobalt oxide on platinum electrode. A four-electrodes amperometric cell is established with the cobalt oxide modified Platinum electrode as working electrode and a pure platinum catalytic electrode as auxiliary electrode (the fourth electrode). The difference of the catalytic ability between the two electrodes, namely the difference (Id) of the current from the working electrode (Iw) and the current from the auxiliary electrode (Ia), is used to determine the concentration of the ammonia selectively. An in situ electrochemical assistant modification method is developed to deposit cobalt solid compound catalyst onto the platinum electrode as long as it can provide high-valence state cobalt.

2. Materials and methods

2.1. Reagents
A porous PTFE membrane (Millipore PTFE membrane, LSWP04700, about 5.0μm pore size, 60% of porosity, size: 60×60mm). Analytical grade Co(NO$_3$)$_2$•6H$_2$O, KNO$_3$, KOH and 25% ammonia solution were obtained from Sinopharm chemical reagent Beijing Co. Ltd. (Beijing, China). Deionized water (18 MΩ cm) was used throughout. Nafion disc (Nafion-117, 12mm in diameter) was purchased from Sigma-Aldrich.

2.2. Instruments
The properties of the sensor are investigated on the Gamry Reference 600 Potentiostat. The reference electrode is saturated calomel electrode (SCE). The electrolyte is saturated KNO$_3$ solution. A dynamic gas distributor is employed to generate various concentrations of ammonia/air mixture. SEM experiments are carried out on a Hitachi S-4800 scanning electron microscope instrument for the morphology of the catalyst. Changing the deposition voltage, the resulted solid precipitations were scrubbed off from the PTFE membrane for XRD analysis on a Purkinje X-2 diffractometer with CuKa radiation.

![Figure 1](image_url)

**Figure 1.** The illustration image of the deposition device (a), the structure of the catalytic electrodes(b) in which a blank area is located between the two electrodes. The structure of the GDE is illustrated in (c).

2.3. Preparation of the gas diffusion electrodes
A porous PTFE membrane was used as basic support and washed with acetone in a Soxhlet extractor for about 4 hours. Two circular sector platinum electrodes, about 100nm in thickness, 10mm in diameter, are sputtered on one side of the membrane, as shown in Figure 1 (b and c). The membrane is cut into 15×20mm chip with the sputtered platinum electrodes at the center. The membrane chip is fixed on the precipitation device.
The precipitation device is shown in Figure 1(a), in which an electrolyte solution reservoir made of Nylon and a gas chamber is installed under the bottom of the electrolyte reservoir. Between the chamber and the reservoir is the porous PTFE membrane with the Pt side faced electrolyte reservoir. The solid catalyst was precipitated on Pt side of the PTFE film and was used as the working electrode. The electrolyte is the mixture solution containing 2.0%wt Co(NO$_3$)$_2$ and 2.0%wt KNO$_3$. Based on introducing 0.10%vol ammonia/air mixture into the precipitation device at about 0.10L/min flow rate and controlling the decapitation voltage at about 0.6V v.s. SCE, the black precipitates were deposited on the other platinum film. The brown-black deposition layer is immersed in deionized water for about 4 hours. After dried at 60°C for 2~4 hours, the GDE is prepared for the sensor.

2.4. **Fabrication of ammonia sensor**

As shown in Figure 2, the Pt reference electrode and counter electrode were sputtered on an alumina substrate. The Nafion film, which had been immersed in saturated KNO$_3$ solution for 8 to 12 hours, was coated on the substrate. Then the GDE membrane was put on the Nafion film with the catalytic side facing the Nafion film. Finally a hot-pressing treatment was carry out under 120°C with a pressure of about 100N/cm$^2$.

In the ageing treatment process, the two working electrodes and the reference electrode are short connected for about 48 hours in air. And then properties of the sensors can be tested.

![Figure 2. The assembly and the structure of the sensor.](image)

3. **Results and discussions**

3.1. **Responses of the sensor**

![Figure 3. (a) The Responses of the sensor to 500ppm ammonia in air. (b) The concentration-current curve.](image)
The sensing characteristics of the sensor towards various concentration of ammonia in air were preliminarily evaluated. The response was calculated as the change of the difference of the currents from working electrode (Iw) and assistant electrode (Ia). It is expressed as \( I_d = I_w - kI_a \) (k is a correction coefficient related to the effective surface area of the assistant electrode). The sensitivity was about 1.2uA/ppm in the range of 0-500ppm. The response speed, which is defined as the time for the response of ammonia to reach 90% of its saturation value (T90, to 500ppm of ammonia in air, ), is about 2 seconds as shown in Figure 3(a). The linear relation between currents and NH3 concentrations could be observed in Figure 3(b). No significant signal degradation was found on the response curve. It suggested that the ammonia sensor showed a very good stability.

3.2. Electrochemical properties of the catalytic electrode
An electrochemical cell was composed with a GDE of 8mm in diameter as working electrode, a saturated calomel electrode (SCE) as reference and Pt plate as counter electrode in 0.1M KNO3 solution. The cyclic voltammogram of the electrode, at a scan rate of 0.1mV/s between 0 to 1.0V, shows a kink point. This kink points at about 0.20V can be observed. This indicated that the oxidization of ammonia is related to the oxidization state of catalytic electrode. At about 0.2 to 0.3V vs. SCE, a oxidation can be found. So, Co(OH)2 is oxidized at this voltage reversibly.

3.3. Morphology of the catalyst

![Figure 4. The morphology analysis of the catalyst layer. (a, b) The SEM images of the catalyst layer and (c) The XRD analysis of the depositions deposited at bias voltage v.s. SCE, 0.60V. (d) The cyclic voltammogram of the catalytic electrode.](image)

In the process of deposition, when ammonia/air mixture gaseous precipitant passed by the hydrophobic side of the porous PTFE film, a blue solid layer can be found deposited on the surface of the other side which had been sputtered with platinum. The thickness of precipitation layer would keep
increasing when there was enough reacting time. After about 2 hours of reaction, with 0.1%vol ammonia air mixture as precipitant gas, the thickness of the oxide layer would reach about 0.35~0.50mm at the deposition voltage of 0.6V. SEM images of the solid precipitation on the electrode, in Figure 4(a) and (b), exhibit some scale-like flakes stacked together in order. The sizes of flakes are uniformly about 0.5um. Additional experiments indicated that, the size of the flakes had no relationship with neither the concentration of the ammonia reaction gas nor the voltage between the two electrodes.

The solid powder was scrub off from the surface of Pt/PTFE porous film for XRD analysis. XRD patterns of the precipitations deposited at 0.60V (v.s. Hg/HgO electrode) were shown in Figure 4(d). XRD indicated that, 0-0.6V, the resulted blue deposition was a mixture mainly Co(OH)2 with little amount of CoOOH (JCPDS: 51-1731 and 02-0925). The coexistence of Co(III) and Co(II) in the hydroxide solid made its catalytic properties similarly to Co3O4 as had been reported. In Figure 4(d), a kink point at 0.2V-0.4V vs SCE indicates the oxidization of Co(II), where the oxidization current related to the concentration of ammonia increased significantly (P1). So, the Co(OH)2/CoOOH couple is regarded as the core catalyst in the working electrode.

3.4. The cross sensitivity

| Gases                | Cross-sensitivity |
|----------------------|-------------------|
| ammonia              | 1                 |
| monomethylamine      | 1                 |
| dimethylamine        | 0.6               |
| trimethylamine       | 0.2               |
| ethylamine           | 0.3               |
| hydrogen             | 0.04              |
| alcohol              | 0.02              |
| Ethylene oxide       | 1.6               |

Table 1. The cross-sensitivity properties of the sensor.

Note 1, The concentration of gas samples are about 10ppm;

A valuable property of this ammonia sensor is the excellent selectivity. It has no reposes to almost all acid gases and some neutral gases, such as hydrogen sulfide, carbon dioxide, methane, butane and alcohol. But it exhibits some response abilities to high reactive gas such as hydrogen and ethylene oxide etc. The relative sensitivity of trimethylamine is about 0.2 when the response to ammonia is 1. Table 1 shows some cross-sensitivities to different gases. The value of cross-sensitivity is compare with the response current to ammonia.

4. Conclusion

The deposition on the platinum electrode is a mixture of cobalt hydroxide and cobalt oxyhydroxide. It is an effective component gives the electrode electrochemical sensing ability. Ammonia diffused to the surface of the electrode, pulls the chemical equilibrium of Co(OH)2/CoOOH to higher valence state. The oxidation current from the working electrode demonstrates a linear relationship with the concentration of ammonia. The obviously different activity to ammonia between the modified platinum electrode and bare platinum electrode can be used to identify ammonia in the air with the existence of interference gas such as hydrogen and hydrogen sulfide. With pure platinum employed as
assistant electrode, the current difference between the working electrode and the assistant electrode had a clear linear correlativity with the concentrations of ammonia in air. The sensors exhibit an excellent selectivity to ammonia no matter in acid environment or basic environment, especially to those reducible gases such as hydrogen and alcohol. The sensor is promising great future in industry application and domestic health care device.

Acknowledgment
This work was supported by the National Natural Science Foundation of China (NSFC, 61771450 and 61831011).

References
[1] Y. Deng, J. D. Englehardt, Electrochemical oxidation for landfill leachate treatment, Waste Manage., 27(2007), pp.380-388.
[2] J. Zhao, Z. Liu, Y. Qin, W. Hu, Fabrication of Co3O4/graphene oxide composites using supercritical fluid and their catalytic application for the decomposition of ammonium perchlorate CrystEngComm, 16(2014), pp.2001-2008.
[3] J. C. Ganley, An intermediate-temperature direct ammonia fuel cell with a molten alkaline hydroxide electrolyte, J. Power Sources, 178(2008), pp.44-47.
[4] N. J. Bunce, D. Bejan, Mechanism of electrochemical oxidation of ammonia, Electrochim. Acta, 56(2011), pp.8085-8093.
[5] H. N. Abid, U. M. Nayef, F. A. H. Mutlak, Preparation and characterization Co3O4 nanoparticles on porous silicon for humidity sensor by photoluminescence, Optik 178(2019), pp. 379-383.
[6] A. Younis, D. Chu, X. Lin, J. Lee, S. Li, Bipolar resistive switching in p-type Co3O4 nanosheets prepared by electrochemical deposition, Nanoscale Research Lett., 36(2013), 8, pp.1-5.
[7] J. Zhou, J. Zhang, A. Ur Rehman, K. Kan, L. Li, K. Shi, Synthesis, characterization, and ammonia gas sensing properties of Co3O4@CuO nanochains, J. Mater. Sci., 52(2017), pp.3757–3770.
[8] M. Khasu, T. Nyathi, D. J. Morgan, G. J. Hutchings, M. Claeysa, N. Fischer, Co3O4 morphology in the preferential oxidation of CO, Catal. Sci. Technol., 7(2017), 4806-4817.