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Rui You

Micromachined Mixed-Potential-Type YSZ-Based Sensors for Nitrogen Dioxide Monitoring in Automobile Exhaust

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Micromachined Mixed-Potential-Type YSZ-Based Sensors for Nitrogen Dioxide Monitoring in Automobile Exhaust

Doctoral Thesis accepted by
Research on key technology of mixed-potential-type NO_2 sensor based on yttrium stabilized zirconia

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Supervisor's Foreword

Under the dome, we share the same fate as breathing. The importance of air to human beings is self-evident. Entering the 20th century, with the rapid development of world industry and the sharp increase in population, the number of motor vehicles keeps increasing. The shortage of resources and the environmental pollution caused by exhaust emissions are becoming increasingly prominent. It has become a severe challenge for the sustainable development of the automobile industry. Nitrogen oxides in exhaust gas are to be blamed because they cause problems such as acid rain, photochemical smog, and ozone hole. They seriously damage the ecological environment and endanger human health. Therefore, many countries in the world have put forward strict limit standards for nitrogen oxides emitted from motor vehicle exhaust. It is necessary to accurately measure and control the nitrogen oxides (mainly NO_2) produced by automobiles.

There are many kinds of gas detection methods. Although instrument analysis methods such as gas chromatography, mass spectrum, and spectrum, have high accuracy, they are complicated to be operated, high in cost, and difficult to be integrated. So, they cannot meet the requirements of in-situ detection of automobile exhaust. With the development of sensor technology and material science, researchers have found that Yttrium Stabilized Zirconia (YSZ), a solid electrolyte material has the advantages of high temperature resistance, high humidity resistance, stable chemical and mechanical properties, etc. Based on this material, gas sensors can not only meet the limit of automobiles' confined space on the instrument use, but also can be better suitable for harsh working environments. They are showing great application potential in the field of high-temperature gas detection.

The theme of this book is the technical research related to gas sensors. The key technologies of mixed potential gas sensors based on YSZ are mainly divided into three aspects: sensitive material, electrochemical reaction process, and device manufacturing process. On the basis of a systematic analysis of the existing research work, the author of this book has extracted the key scientific problems existing in sensors, and has given corresponding solutions and verifications. As an important medium for the identification and conversion of gas information, sensitive material is the prerequisite for gas-sensitive characteristics of NO_2 sensors. Firstly, starting

from the research of sensitive material, we have carried out research and innovative design on the components and nanostructures of NO_2-sensitive materials, and developed a low-cost, easy-to-synthesize, high-sensitivity, and selectivity gas-sensitive nanocomposite material. It has greatly improved the basic performance of NO_2 sensors. Secondly, the electrochemical reaction process is an important part of the solid electrolyte gas sensor. Based on the mechanism study of the three-phase reaction interface constituted by electrolyte, sensitive material, and NO_2gas, we innovatively propose a highly efficient, environment-friendly, and controllable micro-nano structure which can build a large specific surface area, and a micro-nano processing method which can increase the number of active sites of electrochemical reaction. It can be applied to optimize the performance of any kind of solid electrolyte sensor. Finally, we focus on the device manufacturing problems which are less discussed in other research work. Through the combination of traditional ceramic material technology and modern MEMS technology, the YSZ mixed potential gas sensor realizes high consistency and batch processing for the first time. It also has low power consumption and is miniaturized. The device has good flexible and mechanical characteristics and can be applied to gas in-situ detection in high-temperature pipelines. This work has significantly reduced the dependence of current chemical gas sensors on human labor, and plays a very good role in promoting the sensor manufacturing industry.

In conclusion, this book introduces an interdisciplinary research result. It combines research achievements in fields such as instrumental science, material science, electrochemistry, and micro-nano electronics. Meanwhile, both theoretical and experimental works have been taken into consideration, and comprehensive innovative research and detailed demonstration of key technologies of gas sensors have been completed. In this challenging subject, the author of this book has made an outstanding contribution. As a result, the performance and reliability of gas sensors have moved ahead. A new commercial manufacturing scheme for the sensor industry has been explored, taking into account both innovation and practicability. The main purpose of this book is to make the new gas sensor practical as soon as possible. It is also the starting point and direction for future researchers.

Minneapolis, USA Prof. Tianhong Cui
June 2024

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Chapter 1
Introduction

1.1 Background of Research

1.1.1 Significance of Fuel-Powered Automobile Exhaust Detection

Since the twenty-first century, the Chinese economy has increased rapidly and the pace of urban construction at all levels in the country accelerated gradually. Meanwhile, the development of industrial production has brought great pressure to the urban environment, and the problem of urban pollution has become increasingly prominent. Of all the environmental pollution, air pollution is the most closely related to human life and should be paid great attention to. According to the data in the *Report on the State of the Environment in China 2016* issued by the Ministry of Ecology and Environment of the People's Republic of China, 254 of 338 cities at prefecture level and above nationwide failed to meet the national air quality standard, accounting for 75.1% [1]. In recent years, the frequent occurrence of smog, PM2.5, and other words in media reports, as well as the frequent occurrence of respiratory diseases in the urban population, have pushed the air pollution problem to the forefront and become the most important urban air pollution problem in Beijing even the whole country [2, 3]. The major air pollutants commonly referred to include: fine particulate matter (PM2.5), inhalable particulate matter (PM10), nitrogen dioxide (NO_2), sulfur dioxide (SO_2), carbon monoxide (CO), and ozone (O_3). These pollutants not only affect the ecological environment but also directly endanger human health. The main pollutants that have a larger impact on human health include: particulate matter, SO_2, and NO_x. Inhalable particulate matter contains many toxic substances and is also the carrier of other pollutants. If it enters the respiratory tract of the human body, it will irritate and corrode the lung wall, thus causing bronchitis, asthma, and other diseases. If SO_2 dissolves in water, it forms sulfurous acid (the main component of acid rain). It is easily absorbed by the mucosal surface of the human body and generates strong

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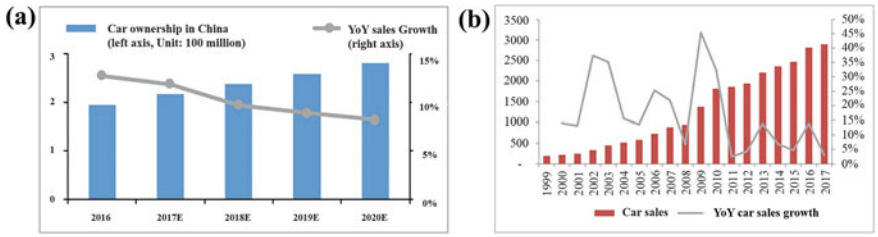

Fig. 1.1 **a** The car ownership and sales growth of China; **b** The car sales and growth rate of China over the years [7]

irritation, thus causing severe respiratory tract disease. But NO_x is more serious. A small amount of NO is easily combined with hemoglobin. It is more likely to cause hypoxia and nerve paralysis than what CO does. NO_2 can be an element of the photochemical reaction in the atmosphere, forming photochemical smog (the main source of PM2.5). It also can cause air pollution problems such as acid rain and ozone hole. The national health department (OSHA, ACGIH) stipulates that the maximum allowable concentration of NO_2 is 1 ppm. When the concentration is higher than 5 ppm, it will cause irritation to mucous membranes and slight discomfort. But when the concentration is higher than 100 ppm, it may cause respiratory disease and even death. This will seriously endanger human health [4, 5].

Nitrogen oxide pollution sources in urban air are mainly generated by fuel combustion. Compared with traditional industrial air pollutant emissions, nitrogen oxide emission from fuel-powered automobiles is dominant, special, and serious [6]. For the Chinese, the population base is large and grows fast. Therefore, the car ownership is high. Car ownership in China exceeded 200 million by 2017, accounting for 20% of the world's total; from 2006 to 2017, the compound annual growth rate of car sales was 15.3% and will continue to grow in the future, as shown in Fig. 1.1. The rapid growth of pollution sources has further worsened the air pollution, endangering the ecological environment and human health.

On the other hand, according to the *2017 Annual Report on Vehicle Exhaust Emission Control* released by the Ministry of Ecology and Environment of the People's Republic of China, the total amount of exhaust pollutants emitted by motor vehicles is estimated to be nearly 44.725 million tons in 2016, while the major pollutants NO_x and PM particles are calculated to be 5.778 million tons and 534 000 tons, respectively, accounting for 90% of the total air pollutants, especially those generated by heavy-duty diesel vehicles (HDDV) [8]. According to the statistical analysis of data in the *2017 Annual Report on Environmental Management of Motor Vehicles in China*, China has been the top producer and seller of motor vehicles in the world for eight straight years, and as a result, automobile exhaust has become an important source of air pollution and shows an increasing trend year by year, as shown in Fig. 1.2. So, it is increasingly pressing to prevent and control vehicle pollution. Because the working condition of an automobile engine is complicated, and it is often operated in moving status, it is extremely difficult to detect and treat automobile exhaust. In

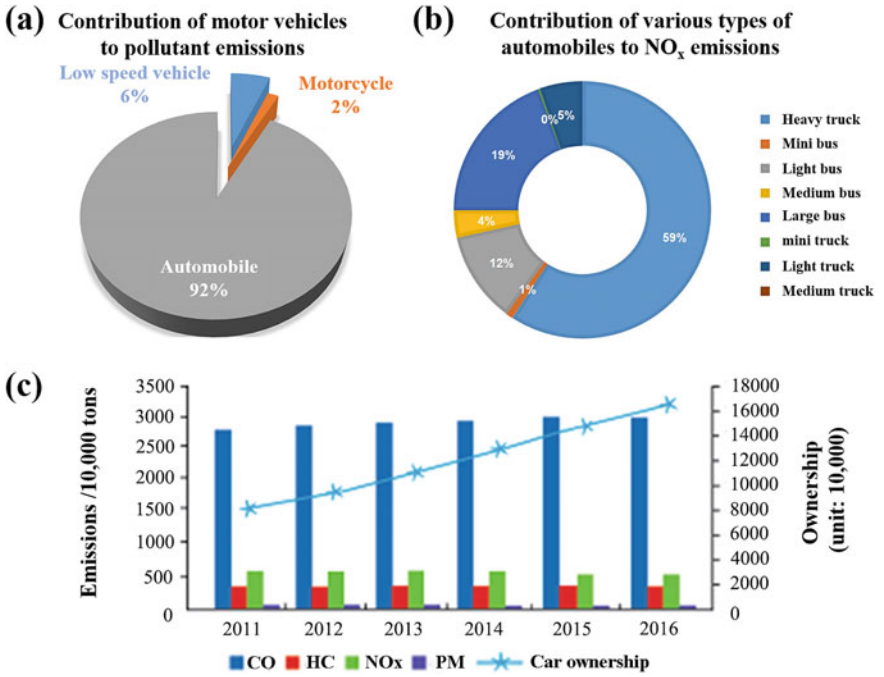

Fig. 1.2 **a** The statistics of the contribution of motor vehicles to NO_x emission in 2017; **b** The contribution of various types of automobiles to NO_x emissions; **c** The growth trend of vehicle pollutant emission in China [9]

addition, most detection methods cannot meet the requirements of online detection of automobile exhaust due to the actual cost and the limited space of the automobile. Therefore, it is significant to study the detection of NO_2 pollutants in automobile exhaust.

In summary, automobiles have become the primary mobile pollution source in modern developed cities and a social consensus has been reached on energy saving and emission reduction of automobiles. Therefore, developing energy-saving and new energy vehicles is an inevitable solution for the society today. However, with a market share of less than 2%, now new energy vehicles are still in the infancy of development in China. An independent and controllable complete energy-saving automobile industry chain is not expected to be formed until 2025. Therefore, the current work is still focusing on strict monitoring and control of the exhaust emissions of existing fuel vehicles.