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Note

Fabrication of Flexible Micro CO Sensor for Proton Exchange Membrane Fuel Cell Applications

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Carbon monoxide poisons the catalyst of the proton exchange membrane fuel cell (PEMFC) subsequently degrading the fuel cell performance. The molecular bond of platinum (Pt) in the catalyst electrode will be seized by carbon monoxide. The transformation of hydrogen molecules into hydrogen ions decreases fuel cell performance. The size of the hole in the gas diffusion layer (GDL) affects the energy of the gas fuel supply; that is, providing an excessive amount of hydrogen wastes energy, whereas providing an insufficient amount of hydrogen decreases catalyst effectiveness. Therefore, this work applied the micro-electro-mechanical systems (MEMS) technology to develop flexible micro CO sensors. The advantages of flexible micro CO sensors include their flexibility, against breakage and ability to be placed anywhere in a fuel cell.

Keywords: Flexible micro CO sensor; PEMFC; MEMS.

1. INTRODUCTION

In recent years, the oil price rises continuously, the global energy is about to be exhausted, looking for alternative energy sources has become a very important subject in the world. Therefore, the fuel cell is paid increasing attention to for its high energy conversion efficiency and harmless emissions and extensive range of application. However, using H_2 as fuel in the proton exchange membrane fuel cell (PEMFC) has several constraints, because the H_2 is usually produced by water electrolysis, the byproduct of the reaction process is CO. In order to reduce the CO content, the water gas shift reaction and low temperature preferential oxidation can be used, the obtained CO concentration is 10-50 ppm. However, even a low CO content degrades the performance of fuel cell apparently [1-5]. Spallina [6] presented an assessment of the impact on solid oxide fuel cell (SOFC) performance prediction of the effect of the combined electrochemical oxidation of CO and H_2, proposing additional analyses to delve into the effects of different steam methane reforming (SMR) and water gas shift (WGS) kinetics models, along with the risk of carbon deposition. Oh [7] investigated the effects of CO poisoning on the performance of high-temperature proton exchange membrane fuel cells (HT-PEMFCs) with phosphoric acid (PA)-doped polybenzimidazole (PBI) membranes. Pedersen [8] presented up-to-date benchmarking methods for testing electrocatalysts for polymer exchange membrane fuel cells (PEMFCs), using the rotating disk electrode (RDE) method. Hu [9] showed that platinum-gold nanoalloy (PtAu/GNR) has much superior catalytic activity and higher poisoning tolerance than the monometal composite catalyst.

CO concentration concerning the real environmental circumstances inside the proton exchange membrane fuel cell is still unable to be obtained in a complete, real-time and accurate manner due to the current monitoring technology bottleneck, which can only be estimated indirectly by way of external measurement, theoretical evaluation or simulation analysis and other methods. Therefore, this study uses tin dioxide as gas-sensing thin film, and uses micro-electro-mechanical systems (MEMS) to develop flexible micro CO sensor to monitor the CO concentration. The advantages of this technology include (1) very small volume; (2) flexible measurement position and accurate embedding; (3) high measurement accuracy and sensitivity and quick response; (4) customized design and development.

2. INTRODUCTION TO MICRO CO SENSOR

2.1 Gas sensor

The gas sensor technology has developed from traditional ceramics and liquid electrochemical techniques into thick film, thin film and semiconductor technologies gradually, even MEMS technology now. At present, the gas sensors on the market mostly use ceramic as substrate, produced by crazing and sintering. The sensitivity is good, but the single-unit production is inapplicable to mass manufacture, so the prices are high, and the thermal response time or gas response time is a little long, reducing the practicability. Therefore, the production mode of gas sensor is combined with the present semiconductor industry in this study, the micro-electromechanical process is used to produce the flexible micro CO sensor, aiming to develop a gas sensor with low cost, low reaction temperature, high sensitivity, quick thermal response and gas response.

2.2 Brief introduction to characteristics of tin dioxide as gas-sensing thin film material

The gas-sensing thin film used in this study is SnO_2, it is the most suitable gas-sensing material for its sensitivity to hydrocarbon compounds, stable voltinism and high production compatibility. The SnO_2 based oxide is one of the most extensively used materials. Because the SnO_2 can work at a low operation temperature, and it has relatively high sensitivity at the operation temperature. However, besides sensitivity, the principal characteristics of gas sensor include stability, repeatability and selectivity. There are oxygen adsorption and desorption at an appropriate operating temperature, and the sensitivity to different gases varies with the temperature. An appropriate temperature range can accelerate the reaction, shortening the response time of SnO_2 to reducing gas. At a low working temperature, the adsorption and desorption reactions on the material surface are too slow. If the working temperature is too high, the reducing gas desorption is influenced, so that the measurement result is influenced. An appropriate addition of catalyst can reduce the reaction temperature and increase the response and recovery time and selectivity. Certainly, high sensitivity, quick response and repeatability are essential conditions of good gas sensors.

2.3 Introduction to sensing principle of micro CO sensor

Among the CO gas sensors, the commercialized CO gas sensors include (1) constant potential amperometry type sensors; (2) semiconductor type sensors and (3) catalytic combustion type sensors. This study uses semiconductor type gas sensor for its high sensitivity and quick response. The sensing principle of the sensing metal layer is that a space-charge region is formed on the surface of metal oxide grains, resulting in electron transfer, forming an electron depletion layer on the surface. When the CO gas passes, the CO molecules are adsorbed, so that the resistance is changed, measurable signals are generated. In terms of electrode, the platinum is used as electrode material, because the platinum has stable properties and it is unlikely to oxidize. In various literatures, the sensitivity of CO gas sensor is related to the gas temperature. Therefore, a microheater is integrated within the sensing range of CO gas sensor as compensation without influencing the operation of fuel cell, so that the detected gas temperature is increased, the sensitivity can be enhanced.

3. PROCESS OF FLEXIBLE MICRO CO SENSOR

The MEMS technology is used to develop the flexible micro CO sensor on the PI flexible substrate, the thickness is 50μm. The PI polymer is characterized by high temperature resistance, compression resistance, high flexibility and good durability.

The production process is shown in figure 1, including the following steps: (a) The PI substrate is cleaned with acetone and methanol organic solutions, the residual methanol is removed by DI water, and the surface dust and residual oil and fat are removed, so as to enhance the adhesive ability of thin film metal; (b) The Cr is evaporated as the adhesion layer between Au and lower insulating layer, enhancing the adhesion between Au and PI; (c) Exposure and development define the sensing pattern of micro CO sensor; The pattern is transferred by wet etching to the metal film of Cr and Au; (d, e) The SnO_2 is evaporated on the PI one side with pattern defined as gas sensing layer; (f) Finally, PI 7505 is spin coated on the flexible micro CO sensor to complete the protective layer. The real product and optical micrograph are shown in figure 2.

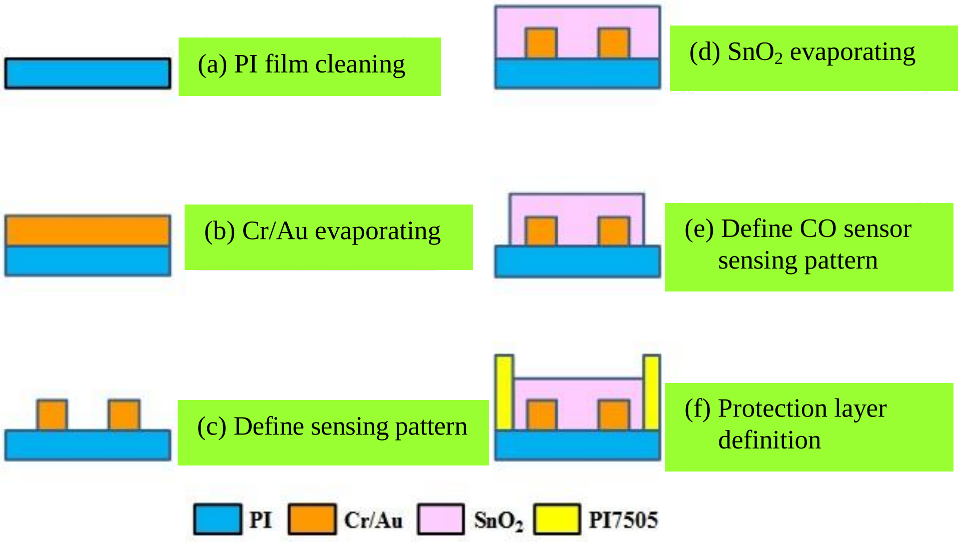

Figure 1. Process of flexible micro CO sensor.

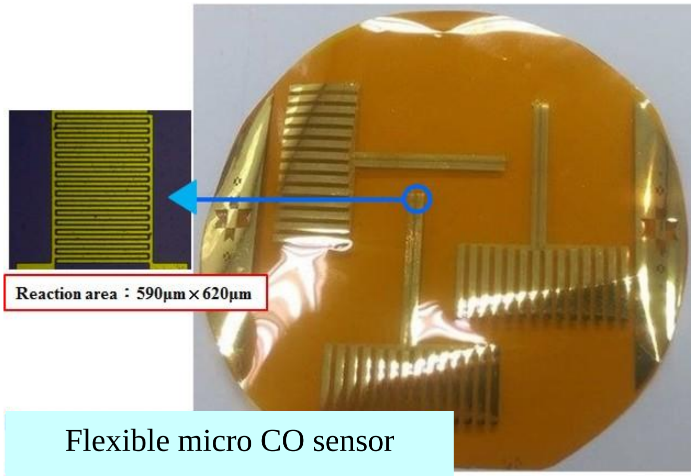

Figure 2. Real product and optical micrograph of flexible micro CO sensor.

4. CORRECTION OF FLEXIBLE MICRO CO SENSOR

The micro CO sensor shall be corrected before it is embedded in the fuel cell to measure signals. The correction relation must be created for each micro CO sensor, because the data (sensitivity, resistivity range) of CO concentration corresponding to the resistivity in the measurement of fuel cell can be obtained from the relation between resistivity of micro CO sensor and CO concentration.

In terms of the correction of micro CO sensor, 10, 50 and 100 ppm commercial CO gas cylinders are led in one runner of a fuel cell in turn, the schematic of correction is shown in figure 3. The resistivity of micro CO sensor is measured when the concentration changes, the measured resistivity is read by LCR measuring instrument in the process, and the correction curve is drawn, as shown in figure 4. The advantages of flexible micro CO sensors include their flexibility, against acidic environment and ability to be placed anywhere in a proton exchange membrane fuel cell.

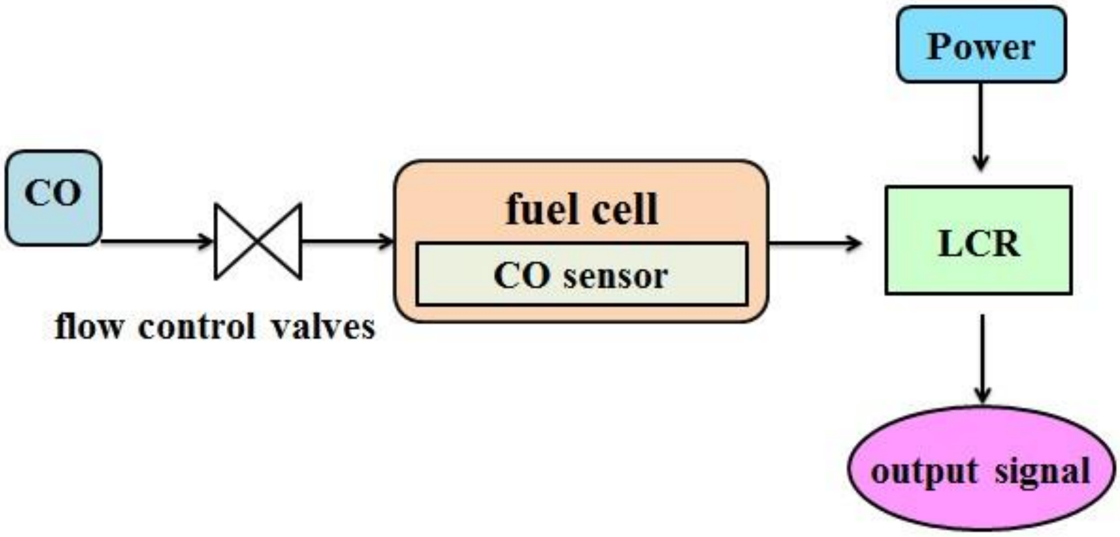

Figure 3. Schematic diagram of correction of micro CO sensor.

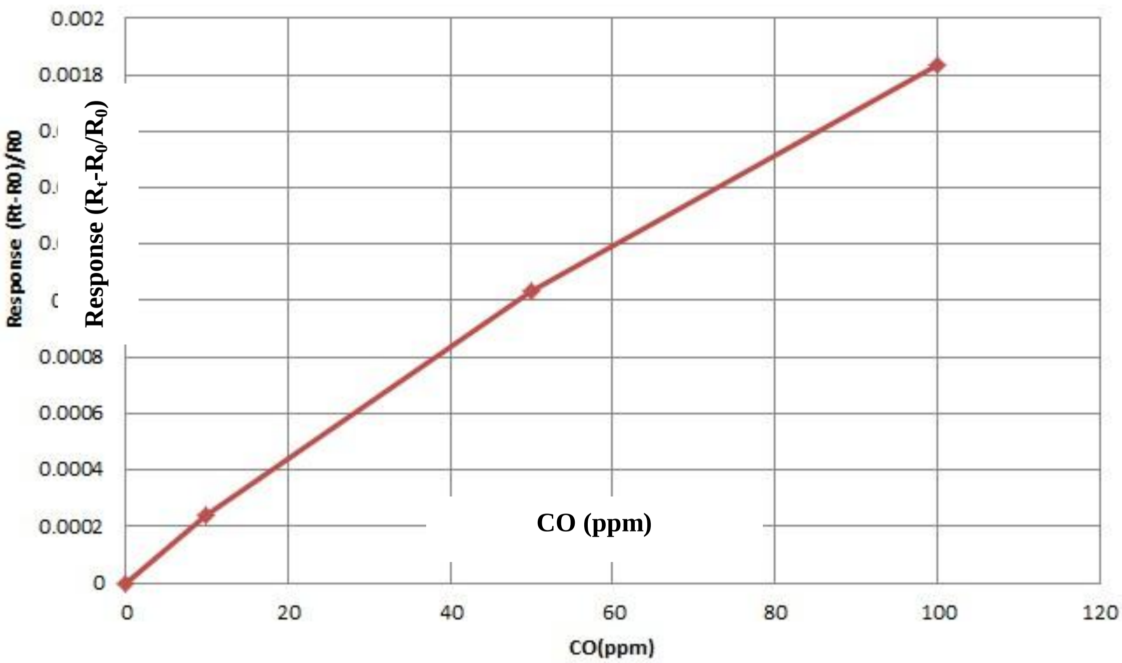

Figure 4. Correction curve of micro CO sensor.

5. CONCLUSION

This study used MEMS technology to develop a flexible micro CO sensor on PI substrate successfully, it is characterized by free plugin, high accuracy, high linearity, high sensitivity, flexibility and robustness, batch manufacturing and quick response. The CO concentration is corrected for the flexible micro CO sensor. The experimental results prove its reliability and linearity. The flexible micro CO sensor can be embedded in the low temperature fuel cell (figure 5) for local measurement in the future, so that the internal microscopic diagnosis information can be fed back to the user accurately for operation management, and the internal reaction information when the low temperature fuel cell is in operation can be known completely, so as to improve the performance and life of low temperature fuel cell.

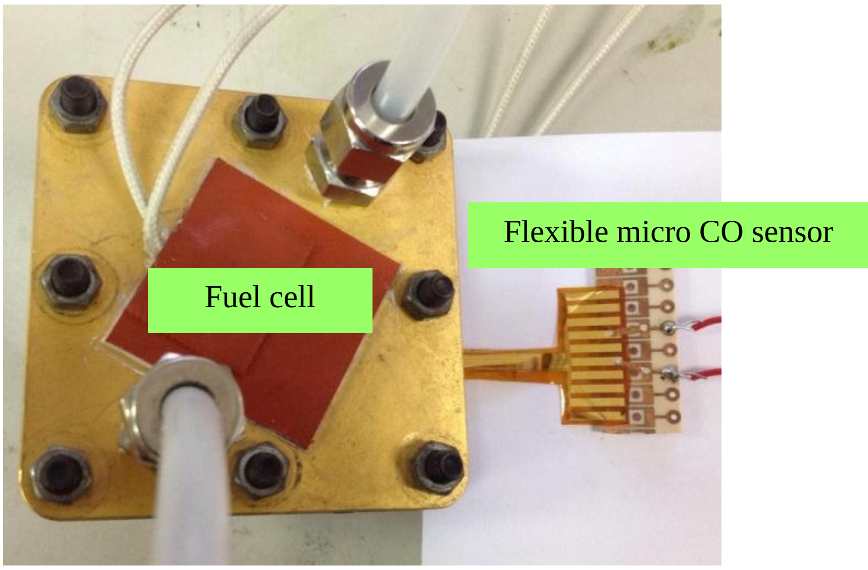

Figure 5. Stereogram of fuel cell embedded with flexible micro CO sensor.

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References

1. S. J. Lee, S. Mukerjee, E. A. Ticianelli and J. McBreen, *Electrochimica Act*a, 44 (1999) 3283-3293.
2. L. Y. Sung, B. J. Hwang, K. L. Hsueh and F. H. Tsau, *Journal of Power Sources,* 195 (2010) 1630-1639.
3. T. Kadyk, S. Kirsch, R. H. Rauschenbach and K. Sundmacher, *Electrochimica Acta,* 56 (2011) 10539-10602.
4. T. V. Reshetenko, K. Bethune, M. A. Rubio and R. Rocheleau, *Journal of Power Sources,* 296 (2014) 344-362.
5. L. Y. Sung, B. J. Hwang, K. L. Hsueh, W. N. Su and C. C. Yang, *Journal of Power Sources*, 242 (2013) 264-272.
6. V. Spallina, L. Mastropasqua, P. Iora, M. C. Romano and S. Campanari, *International Journal of Hydrogen Energy,* 40 (2015) 15012-15031.

7. K. Oh and H. Ju, *International Journal of Hydrogen Energy*, 40 (2015) 7743-7753
8. C. M. Pedersen, M. Escudero-Escribano, A. Velázquez-Palenzuela, L. H. Christensen, I. Chorkendorff and I. E. L. Stephens, *Electrochimica Acta*, 179 (2015) 647-657.
9. X. Hu, C. Lin, L. Wei, C. Hong, Y. Zhang and N. Zhuang, *Electrochimica Acta*, 187 (2016) 560-566.

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