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New sensor for gases dissolved in transformer oil based on solid oxide fuel cell

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ABSTRACT

Due to the poor anti-jamming performance, less gas species, low detection accuracy, short life, medium leaking or carbon monoxide poisoning and other defects that current sensors for gases dissolved in transformer oil have, a SOFC-based multi-component gas sensor has been designed. The physical, chemical and electrochemical mechanisms of gases in the SOFC have been analyzed, and the mathematical model which contains the static, dynamic and load effects has been established. And the model parameters have been optimized in this paper. The results showed that: (1) temperature is the decisive factor for the static characteristic of the sensor, and the accuracy of temperature should be controlled within ± 0.1 °C to achieve the 0.1 μL/L detection limit of C_2H_2. (2) The polarization resistance is inversely proportional to the input gas concentrations, while the open-circuit voltage is proportional to them. (3) The relationship between the short-circuit current and the square of input gas concentration is direct proportion, and the polarization resistance is the determinant of sensor dynamic characteristics. Finally, a gas experimental system has been built to verify the above conclusions. This gas sensor can realize the high-precision detection for multi-component gases dissolved in transformer oil effectively.

1. Introduction

In EHV (extra high voltage) power equipments, the oil-filled power transformers account for more than 90% of all transformers [1]. Monitoring the gases dissolved in the transformer oil, also known as DGA (dissolved gas analysis), is the best way to ensure the stable operation of power transformers. That is, by monitoring the types, contents and changing trends of dissolved gases, we can analyze the running state of transformers, predict the development trend of fault and implement the state maintenance. And this method is welcomed by the national power sectors. For instance, in China, DGA has been classified as the first one of 32 pre-test projects about oil-filled transformers [2].

Sensors used for monitoring the multi-component trace gases dissolved in transformer oil are mainly classified as follows: (1) Sensors based on the gas sensor array [3]. They have the advantages of small volume and high-speed detection, but the development is hindered by the cross-interference and short life. (2) Sensors based on infrared spectroscopy [4]. The sensitivity of them has been improved, but they cannot detect hydrogen (H_2), oxygen (O_2), nitrogen (N_2) and other symmetrical molecules. Besides, the cost of them is high. (3) Sensors based on photoacoustic spectroscopy [5]. They can obtain 1 nL/L detection limit in the laboratory, but the vibration and noise signal in the operation field will seriously affect the normal photoacoustic detection, leading to a sharp decline of accuracy. Moreover, the cost is also high. (4) Sensors based on chromatographic techniques [6]. Being the most mature gas detecting instruments and widely used in the detection for dissolved gases in transformer oil, chromatographic detectors have been greatly improved, in terms of the detecting accuracy, reliability and cost performance ratio compared with other testing instruments. The thermal conductivity detector (TCD), hydrogen flame ionization detector and catalytic combustion detector are commonly used chromatographic sensors, whose high accuracy, reliability and cost performance ratio can meet the requirements of quantitative detection of gases. But, they are bulky, and have low sensitivity, long reaction time, multiple carrier gases and other shortcomings. Although, the subsequent MEMS (Microelectromechanical Systems)-based TCD [7] has some improvement in the reaction time and dead volume, the detections to some gases have not yet reached the required accuracy of 0.1 μL/L. For example, their detection accuracy on acetylene (C_2H_2) is only 5 μL/L, which is much lower than the critical value 1 μL/L for the occurrence of fatal faults of electrical equipments. Therefore, developing a kind

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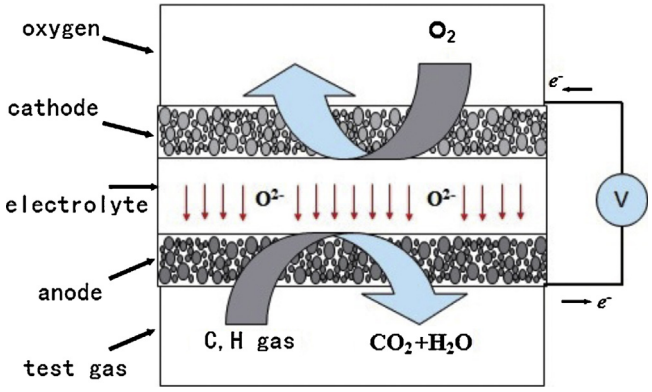

Fig. 1. Sectional view of working process of SOFC gas sensor.

of trace gas sensor that can measure multi-component trace gases (especially H_2 and hydrocarbon gases) with high sensitivity, good reliability and long service life, is urgent.

Solid oxide fuel cell (SOFC) is a new type of fuel cell, which has been valued in the fields of clean [8], portable devices [9], electric vehicles [10], civilian fixed station of CHP (combined heat and power) system [11], and efficient distributed generation system [12]. It uses solid electrolyte to solve the common problem about electrolyte leakage in the liquid fuel cell, and uses high temperature to settle the carbon monoxide (CO) poisoning problem [13]. Compared with traditional fuel cells, SOFC using zirconia (ZrO_2) electrolyte has the characteristics of fuel diversity, and this feature is very suitable for the multi-component gas detection. In the previous study of the SOFC multi-component gas detection, we have analyzed the static and dynamic characteristics of gases in SOFC, predicted the detection voltage of multi-component gases, and proved SOFC to be a linear integral type gas sensor [14].

Meanwhile, to further understand the working mechanism of SOFC, all kinds of mathematical models have been built and studied. Sorrentino et al. have studied the models based on physics and chemical processes of SOFC [15], and equivalent circuit models based on impedance spectroscopy have been put forward by Huang et al. [16], Leonide et al. [17] and Lang et al. [18]. Besides, the SOFC control models based on Hammerstein [19], artificial neural network [20] and ANFIS identification [21] have also been studied. All these research results provide theory support for the SOFC power and sensor, but most of them only consider few fuels, such as H_2, CO and methane (CH_4). In this article, a SOFC-based gas sensor was designed. By analyzing the physical, chemical and electrochemical mechanism of the gases in SOFC, we decomposed the sensor into three parts: static, dynamic and fluid losses. Then, a complete mathematical model considering temperature, pressure, polarization loss, Ohmic loss and gas mass loss was established, in which the model parameters were extracted and optimized. Finally, the relevant experimental system was built to validate the model and parameters.

2. Establishment of SOFC gas sensor model

Fig. 1 shows the cross-sectional view of a SOFC gas sensor in working, which contains five parts: anode, electrolyte, cathode, combustible gas channel and air channel. Taking H_2 for example, it starts with the ion reaction at the anode, generating hydrogen ions and electrons. Then, the electrons reach the cathode through the load circuit and ionize the O_2 in the cathode air, generating oxygen ions. Finally, the generated oxygen ions pass through the cathode and electrolyte to react with hydrogen ions at the anode, generating water vapor. This is a complete oxidation–reduction reaction, which achieves a direct conversion between chemical energy and electrical energy. Each reaction generates two free electrons, and they do work through the external circuit. Thus, we can measure the power of peripheral circuits to obtain the amount of hydrogen consumption.

There is an essential difference between the operating principles of the SOFC gas sensor and ZrO_2 oxygen sensor, though both of them use ZrO_2 as the dielectric. The ZrO_2 oxygen sensor can obtain the concentration of O_2 through Nernst equation, while the SOFC gas sensor must take all the physical, chemical and electrochemical processes of gas reaction into account, and establish the mathematical model involving the static, dynamic, and load effects. In order to obtain the static model of SOFC gas sensor, assume the model parameters are independent, and the model would be analyzed by using the combination principle [22]. Firstly, we analyze the reversible output voltage under the ideal working condition. Secondly, we consider the independent effects of temperature, pressure and reference gas, respectively. Thirdly, we use the linear combination to give the comprehensive output voltage. Finally, we obtain the comprehensive model by mixing the static one with the dynamic one.

The ideal working conditions for the SOFC gas sensor are as follows:

1) standard temperature;
2) standard atmospheric pressure;
3) pure O_2 as the reference gas;
4) the pure combustible gases injected into the device;
5) the parasitic reaction of gases not considered to ensure sufficient burning.

Under these ideal work conditions, the output voltage of SOFC gas sensor is the reversible voltage E_r, which is

$$E_r = -\frac{\Delta G_0}{nF} = -\frac{\Delta H_0 - \theta \Delta S_0}{nF}, \tag{1}$$

where ΔG_0, ΔS_0 and ΔH_0 are the Gibbs free energy change, entropy change and enthalpy change in standard state, respectively, n is the amount of generated electrons, F is the Faraday constant 96485.3383 C/mol, and θ is the Debye temperature.

As SOFC works in the high temperature environment (500–800 °C), we should consider the impact on the reversible voltage when temperature increases. Taking the derivative of temperature in (1), the proportional relation k_θ between the quiescent voltage and temperature is

$$k_\theta = \frac{\Delta S_0}{nF}. \tag{2}$$

Then, the thermodynamics voltage variation ΔE_θ can be given as

$$\Delta E_\theta = k_\theta(\theta - \theta_0) = \frac{\Delta S_0}{nF}(\theta - 273.15), \tag{3}$$

where θ_0 is the standard temperature 273.15 K.

Because gas pressure of the output port is a standard atmospheric pressure, the long separation column channel is used to separate the mixed gases to pure gases one by one, where the input port gas pressure must be set to about 0.12 MPa to ensure sufficient burning, and the output rate of flow is ranging from 30 mL/min to 90 mL/min at the same time. When the pressure increases, the output voltage increment ΔE_p for the chemical reaction $k_1X + k_2Y \rightarrow k_3K + k_4M$ is given as

$$\Delta E_p = -\frac{R\theta}{nF} \ln \frac{(p_K/p_0)^{k_3}(p_M/p_0)^{k_4}}{(p_X/p_0)^{k_1}(p_Y/p_0)^{k_2}}, \tag{4}$$

where p_X, p_Y and p_K, p_M are the partial pressure of the reactants and products, respectively, p_0 is the standard pressure, the subscripts