Influence of Heat Disturbance on the Performance of YSZ based CO$_2$ Sensor with Compound of Li$_2$CO$_3$-BaCO$_3$-Nd$_2$O$_3$ as Auxiliary Sensing Electrode

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ABSTRACT

Suddenly changes and fluctuations of temperature often occur in the operational environment of the CO$_2$ electrochemical sensor. In this work, the YSZ based potentiometric CO$_2$ sensor having Li$_2$CO$_3$-BaCO$_3$-Nd$_2$O$_3$ compound as its auxiliary sensing material was prepared. And the effects of several types of heat disturbance on the performance of this kind of sensor ware studied. The results indicate that the sensors after heat disturbances respond similarly with the sensor as prepared, which presents rapid and correct response for the change of CO$_2$ concentration within the experimental range of 271-576802 ppm. The sensors, with or without heat disturbance, respond well as different extents of abrupt alteration of CO$_2$ concentration occurs, and the EMF outputs recover rapidly as the concentration of CO$_2$ change back to the base value. At the constant concentration of CO$_2$, the EMFs of the sensors with or without heat treatment decrease slowly as the time increases, the reason for this phenomenon might be the accumulation of inert substances on the electrode interfaces and ageing of electrodes. However, heat treatment can improve the long-term stability of the sensor to some extent. Furthermore, this type of sensor works stably with the existence of water vapor (10%), it has similar response curve in the dry and water vapor content system. After some further investigations and improvements, it might be potentially applied in the practical combustion atmosphere.

Keywords: heat disturbance, YSZ, CO$_2$ sensor, water vapor

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1. INTRODUCTION

The potentiometric CO$_2$ sensor can be prepared by using YSZ as the solid electrolyte, and, carbonates or carbonate content compounds as the auxiliary sensing materials [1-4]. YSZ is an excellent conductor for oxygen anions at elevated temperatures, so the YSZ based CO$_2$ sensors prefer to working in the atmospheres with high temperature, such as the flue gas of power plants. As we know, flue gas is the gaseous emission after the oxidative combustion of fossil fuels, which mainly composes of CO$_2$, O$_2$, N$_2$, SO$_2$, CO, water vapor and various solid particles [5-7]. As a result, constantly operation at high temperatures is required for the CO$_2$ sensor in the flue gas environment. Meanwhile, the sensor should not be obviously affected by the abrupt alteration or frequently fluctuation of temperature [8, 9].

During the operation of YSZ based CO$_2$ sensor, the CO$_2$ in the detecting system reacts with the auxiliary sensing electrode, and simultaneously the co-existing oxygen gas is reduced at the reference electrode. These electrochemical processes can be finally presented by the electromotive force (EMF) of the sensor. Temperature correlates with the electrochemical parameters and mechanisms of the processes, as a result, the abrupt alteration or fluctuation of the temperature which frequently occurs in the practical operation environment, probably affects the performance of the sensor [10-12]. Futata et al. [13] studied the effects of heat treatment on the solid electrolyte CO$_2$ sensor, and found that pulse heat treatment caused the recovery of the deteriorated sensor, but the extent of recovery correlated with the temperature and time of the pulse heat treatment. With the pulse heat treatment of the sensing electrode (carbonates) to near its melting point, the deterioration of the sensing electrode caused by the aging or reaction with other substances could be recovered and reactivated. Miyachi et al. [14] used Nasicon and compound of Ni$_2$CO$_3$-BaCO$_3$ to prepare potentiometric CO$_2$ sensor, and found the deterioration of the response caused by the aging could be recovered by some extent of heat disturbance. Yamauchi et al. [15] investigated the reactivity and stability of the system of compound made up of oxides of rare metal and Li$_2$CO$_3$, and the results indicated that the temperature of heat treatment strongly affected the structure of the compound.

Considering the practical operation environment of the CO$_2$ sensor, this study investigated the effects of several types of heat disturbance (long-term heat treatment and abrupt temperature alteration) on the performance of the YSZ potentiometric CO$_2$ sensor with the compound of Li$_2$CO$_3$-BaCO$_3$-Nd$_2$O$_3$ as the auxiliary sensing material. The experimental results indicate that the potentiometric sensor respond rapidly and correctly to the change of CO$_2$ concentration in the experimental range of 271-576802 ppm although after different types of heat disturbance. The sensors, with or without heat disturbance, respond well as different extents of abrupt alteration of CO$_2$ concentration occurs, and the EMF outputs recover rapidly as the concentration of CO$_2$ changes back to the base value. At the constant concentration of CO$_2$, the EMFs of the sensors with or without heat treatment decrease slowly as the time increases, the phenomenon probably was caused by the accumulation of inert substances on the electrode interfaces and ageing of electrodes. However, heat treatment can improve the long-term stability of the sensor to some extent. The sensor we prepared not only
exhibits good resistance for heat disturbances, but also works stably with the existence of water vapor (10%). After some further investigations and improvements, this type of sensor might be potentially applied in the practical combustion exhaust gas atmosphere.

2. EXPERIMENTAL

2.1 Device preparation

The YSZ electrolytes were prepared by slip casting method from powders of ZrO$_2$+8mol% Y$_2$O$_3$ (TOSOH TZ 8Y) and sintered at 1500 °C, which were discs shaped of 10 mm diameter and 2 mm thickness [16]. Its surfaces were polished with a 3000 waterproof alumina abrasive paper and cleaned by successive rinsing with hydrochloric acid, warm n-pentane, acetone, and demineralized water in an ultrasonic bath [17]. The powder of Li$_2$CO$_3$, BaCO$_3$, Nd$_2$O$_3$ were weighted according to the mole ratio of 1:1:1, and then were milled in the planetary micro mill for 2 h using a slurry with acetone. Subsequently, the slurry was painted on the surface of one side of the YSZ disc and then dried at 70 °C. Subsequently, calcined at 750 °C for 50 min under the atmosphere of pure CO$_2$ and then the Au paste (Kunming Institute of Precious Metals, China) was painted on the surface of the YSZ disc and then dried at 700 °C for 2 hours in air. The prepared CO$_2$ sensor was schematically presented in Figure 1.

![Figure 1. Structural schematic of the prepared CO$_2$ sensor](image)

2.2 Electrochemical theory

The prepared YSZ potentiometric CO$_2$ sensor can be written as

CO$_2$, O$_2$, Au | Li$_2$CO$_3$-BaCO$_3$-Nd$_2$O$_3$ | YSZ | Au, O$_2$, CO$_2$  

(1)

At the interface of Au/Li$_2$CO$_3$-BaCO$_3$-Nd$_2$O$_3$, the CO$_2$ and O$_2$ contained in the detecting system react with the Li$_2$CO$_3$ and BaCO$_3$ in the compound of Li$_2$CO$_3$-BaCO$_3$-Nd$_2$O$_3$, which acts as the auxiliary sensing material for the CO$_2$ gas, the related reactions can be presented in equation (2) and (3).

Li$_2$CO$_3$=2Li$^+$+CO$_2$+1/2O$_2$+2e$^-$  

(2)

BaCO$_3$=Ba$^{2+}$+CO$_2$+1/2O$_2$+2e$^-$  

(3)

At the interface of Au/YSZ, oxygen gas in the detecting system is reduced as shown in equation (4).

1/2O$_2$+2e$^-$=O$^2-$  

(4)

At the interface of Li$_2$CO$_3$-BaCO$_3$-Nd$_2$O$_3$/YSZ, Li$^+$ and Ba$^{2+}$ react with the oxygen anions come across the YSZ. The related reactions can be presented in the equation (5) and (6), and the general reactions of the sensor were shown in the equation (7) and (8).

2Li$^+$+O$^2-$=Li$_2$O  

(5)

Ba$^{2+}$+O$^2-$=BaO  

(6)

Li$_2$CO$_3$=CO$_2$+ LiO  

(7)

BaCO$_3$=CO$_2$+ BaO  

(8)

The theoretical transference electrons are 2 in the above equations, as a result, the electromotive force of the prepared CO$_2$ sensor can be presented as equation (9).

\[ EMF=E_0+\frac{2.303RT}{2F}\ln\left(\frac{P_{O_2}}{P_{CO_2}}\right)^{1/2} \]

(9)

In this work, the CO$_2$ sensor is surrounded by the atmosphere of the detecting system. So, both the auxiliary sensing electrode and the reference electrode have the same oxygen partial pressure. As a result, the equation (9) can be simplified as equation (10).

\[ EMF=E_0+\frac{2.303RT}{2F}\ln\left(\frac{P_{O_2}}{P_{CO_2}}\right) \]

(10)

Equation (10) is the detection mechanism of this type of CO$_2$ sensor. By the measurement of the electromotive force of the sensor, the quantity of CO$_2$ in the system can be determined.

2.3 Detection method

The prepared CO$_2$ sensors were pretreated by several types of heat disturbance according to Table 1. During the subsequent CO$_2$ response measurement, the Au paste electrodes were pressed by two Au nets, and conducted by two Au wires (diameter of 0.2 mm) connected to the outside voltmeter. The test sensor was fixed at the center of the reactor, with its sensing electrode and reference electrode exposed to the same atmosphere. The reactor was set up in a tube furnace and each electrode wire was taken out through an Al$_2$O$_3$ tube and contacted with the voltmeter of 34410A for the electromotive force measurement. The measuring temperature was 450 °C, which was given by a K-type (NiCr-NiAl) thermocouple placed in proximity of the sensor and was led out of the furnace through a two-hole alumina tube (Figure 2). The measuring gas was made up of high purity nitrogen and CO$_2$ content gas (balanced by air), and was measured by the high resolution flowmeter (Kyoto 3660).

<table>
<thead>
<tr>
<th>Temperature alteration/°C</th>
<th>Rate / (°C·min$^{-1}$)</th>
<th>Duration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Entry 1</td>
<td>No</td>
<td>-</td>
</tr>
<tr>
<td>Entry 2</td>
<td>450-300-450</td>
<td>10</td>
</tr>
<tr>
<td>Entry 3</td>
<td>450-600-450</td>
<td>10</td>
</tr>
<tr>
<td>Entry 4</td>
<td>450-200-700-450</td>
<td>10</td>
</tr>
<tr>
<td>Entry 5</td>
<td>450-200-700-450</td>
<td>10</td>
</tr>
<tr>
<td>Entry 6</td>
<td>450-200-700-450</td>
<td>10</td>
</tr>
</tbody>
</table>
3. RESULTS AND DISCUSSION

3.1 XRD analysis of the auxiliary sensing compounds

The XRD spectroscopy of the auxiliary sensing compound with or without heat disturbance is presented in Figure 3. According to Figure 3, the compound with several types of heat disturbance (Entry 2: long-term treatment at low temperature, Entry 3: long-term treatment at high temperature, Entry 6: multiple heat disturbance between high temperature and low temperature) have similar characteristics with the compound as prepared (Entry 1). This result indicates that although with different types of heat disturbance, the auxiliary sensing compound of the sensor is hardly changed, and it exhibits good thermal stability.

![Figure 3. XRD diffraction patterns of the auxiliary sensing compound with or without heat disturbance](image)

3.2 Microstructure of the auxiliary sensing compounds

The SEM analysis of the auxiliary sensing compound with or without heat disturbance is presented in Figure 4. Probably due to the complex composition of the auxiliary sensing compound prepared by sintering Li$_2$CO$_3$-BaCO$_3$-Nd$_2$O$_3$ together under the pure CO$_2$ atmosphere, particles with different structure and size contact with each other closely in Figure 4. The auxiliary sensing compound as prepared (Entry 1) has similar microstructure with the auxiliary sensing compound with heat treatment at low temperature (Entry 2). However, the particles enlarged when the auxiliary sensing compound was treated by long-term of high temperature (Entry 3) and multiple heat disturbance between high temperature and low temperature (Entry 6). This result might be caused by the integration of some particles at such a high temperature.

![Figure 4. SEM images of the auxiliary sensing compounds](image)
Influence of Heat Disturbance on the Performance of YSZ based CO\textsubscript{2} Sensor with Compound of Li\textsubscript{2}CO\textsubscript{3}-BaCO\textsubscript{3}-Nd\textsubscript{2}O\textsubscript{3} as Auxiliary Sensing Electrode / J. New Mat. Electrochem. Systems

3.3 Response of the CO\textsubscript{2} sensor

Figure 5 presents the EMF outputs of the sensors during the alteration of CO\textsubscript{2} concentration as the program of 576802→271→576802 ppm. In Figure 5, the EMF curves exhibit relatively symmetrical alteration during the CO\textsubscript{2} decreasing period (576802→271 ppm) and increasing period (271→576802 ppm), respectively. The sensors have very similar EMF values at the same point of CO\textsubscript{2} concentration. As the CO\textsubscript{2} concentration changes abruptly from one point to another one, the EMF value changes correspondingly, and it gets to attain the new stable value after several minutes. According to the experimental results with long-term heat treatment (A) and multiple heat disturbance (B) shown in Figure 5, although with different types of heat treatment (Entry 2: heat treatment of 24 h at 300 ℃, Entry 3: heat treatment of 24 h at 600 ℃, multiple heat disturbance between 200 ℃↔700 ℃ (Entry 4, Entry 5, Entry 6)), the sensors exhibit consistent responses with the alteration of CO\textsubscript{2} concentration, these results indicate that the sensors present good resistance for the heat disturbances.

Figure 6 presents the EMF outputs of the sensor during the alteration of CO\textsubscript{2} concentration as the program of 271→576802→271 ppm, which is the opposite of that shown in Figure 5. Similar with Figure 5, the EMF curves exhibit symmetrical characteristics during the CO\textsubscript{2} increasing period and decreasing period, respectively. Each sensor has the largest EMF output at the highest CO\textsubscript{2} concentration of 576802 ppm, and accordingly, has the smallest EMF value at the lowest CO\textsubscript{2} concentration of 271 ppm. According to the mechanism of this type of sensor, under the same temperature, the EMF value is only determined by the CO\textsubscript{2} concentration in the detecting system. In another word, each CO\textsubscript{2} concentration corresponds to a certain value of EMF response. These assumptions are evidenced by Figure 5 and Figure 6, in which the sensors exhibit consistent EMF outputs at each point with the same CO\textsubscript{2} concentration although under different detection conditions (e.g., different initial CO\textsubscript{2} concentration, during CO\textsubscript{2} increasing period or decreasing period), and with different types of heat disturbance (e.g., 24 h of heat treatment at 300 ℃ or 600 ℃, different times of heat disturbance between 200 ℃↔700 ℃), all of these experimental results imply the good thermal stability of the sensors.
Based on the EMFs in Figure 5 and Figure 6, the correlation of CO$_2$ concentration and its corresponding EMF value can be obtained. Combined this relationship and equation (10), the transference electrons during the continuous change of CO$_2$ concentration can be computed, which are very closed to the theory value of 2. These results indicate that the EMF output of the sensors agrees well with the Nernst characteristic, it is the correct representation of the alteration of CO$_2$ content in the detecting system.

3.4 Repeatability of the sensor

The CO$_2$ concentration in the practical system usually fluctuates or even changes abruptly. In this work, the response of sensor for the abrupt change of CO$_2$ concentration was investigated, and the results are presented in Figure 7. In Figure 7, when the CO$_2$ concentration abruptly changes from the base concentration (576802 ppm) to another value (271321 ppm, 27132 ppm, 2713 ppm and 271 ppm), the EMF outputs of the sensors respond rapidly and get to attain a stable value about several minutes later. After each jump of CO$_2$ concentration, the outputs of the sensors almost recover the original state with the base CO$_2$ concentration, they exhibit good repeatability.

3.5 Stability of the sensor

3.5.1 Long-term stability of the sensor

To understand the stability of the sensor with different types of heat disturbance, the CO\(_2\) response of the sensor with heat disturbances (Entry 2: 24 h of heat treatment at 300 °C, Entry 3: 24 h of heat treatment at 600 °C, Entry 6: 15 times of heat disturbance between 200 °C↔700 °C) and as prepared (Entry 1) were operated under the constant CO\(_2\) concentration of 576802 ppm for 5 days. For the comparison, they also were operated under the constant CO\(_2\) concentration of 271 ppm for 5 days. The experimental results indicate that the EMF of each sensor tends to decrease with the increase of time, and the decreased values are presented in Figure 8. Combined with the SEM detection of the auxiliary sensing compound of Entry 1 and Entry 6 after 5 days of operation (Figure 9), the decrease of the EMF output was probably caused by the deposit of inert substances at the electrode interfaces and the aging of the auxiliary sensing compounds. Obata studied the effects of aging time on the sensor response, and found that the EMF output changed obviously with the increase of aging time, and the reason might be caused by the change of transition film between the sensing material and the solid electrolyte [18]. Shimamoto indicated that the decrease of EMF output might be caused by the change of sensing electrode structure and the diffusion of metal ions to the interface of sensing electrode/YSZ during the operation of CO\(_2\) sensor [19]. Imanaka prepared the CO\(_2\) sensor by using multi-valent ion conductor and YSZ as composite solid electrolyte, and Li\(_2\)CO\(_3\) as auxiliary sensing material, and found that the EMF output of this sensor decreased about 50 mV after operation of 4 days [20].

From the results shown in Figure 8, the sensors exhibit similar long-term stability under these two CO\(_2\) concentrations. And with some extent of heat treatment, the stability of the sensor can be improved accordingly. Compared with the sensor with the heat treatment at high temperature (Entry 3) and 15 times of heat disturbance between 200 °C↔700 °C (Entry 6), the sensor as prepared (Entry 1) and with the heat treatment at low temperature (Entry 2) have a little higher decreased EMF values under the constant CO\(_2\) concentration. This might be due to the similar extent of heat treatment was obtained for Entry 3 and 6. According to the SEM images in Figure 4, probably due to the low temperature of heat treatment (Entry 2) could not change the electrode structure, as a result, it had similar microstructure with the sensor as prepared (Entry 1). However, as the heat treatment intensified (e.g., Entry 3 and Entry 6), the particles enlarged and contacted with each other much more closely, as a result, the EMF tended to stabilize. Belda studied the long-term stability of solid electrolyte CO\(_2\) sensor and indicated that some extent of heat treatment or operation condition affect the stability of sensor response [21].

**Figure 7.** Response of the sensors with abrupt changes of CO\(_2\) concentration

**Figure 8.** Decreased EMF values of sensor after long-term (5d) operation

**Figure 9.** SEM images of the auxiliary sensing compounds after long-term (5 d) operation
3.5.2 Response of the sensor with the existence of water vapor

![Figure 10. Response of the sensors with or without the existence of 10% water vapor](image)

The response of the sensor as prepared (Entry 1) and with 15 times of heat disturbance between 200 °C ↔ 700 °C (Entry 6) were detected in a dry atmosphere and subsequently in a wet atmosphere (10% of water vapor), and the results are presented in Figure 10. According to Figure 10, the sensors exhibit similar EMF curves in both dry and wet atmosphere, and have consistent EMF values at the same values of CO₂ concentration. These results indicate that the sensors prepared in this work have good water vapor resistance, and the heat treatment of multiple times of temperature jumping exhibit neglect effects on the sensor response in such a wet atmosphere.

4. CONCLUSIONS

The YSZ based CO₂ sensor having Li₂CO₃·BaCO₃·Nd₂O₃ compound as its auxiliary sensing material was prepared in this work. And the effects of several types of heat disturbance on the performance of this kind of sensor was studied. The results indicate that the sensors after heat disturbances respond similarly with the sensor as prepared, which presents rapid and correct response for the change of CO₂ concentration within the experimental range of 271-576802 ppm. The sensors, with or without heat disturbance, respond well as different extents of abrupt alteration of CO₂ concentration occurs, and the EMF outputs recover rapidly as the concentration of CO₂ change back to the base value. At the constant concentration of CO₂, the EMFs of the sensors with or without heat treatment decrease slowly as the time increases, the reason for this phenomenon might be the accumulation of inert substances on the electrode interfaces and ageing of electrodes. However, heat treatment can improve the long-term stability of the sensor to some extent. Furthermore, this type of sensor works stably with the existence of water vapor (10%), it has similar response curve in the dry and water vapor content system. After some further investigations and improvements, it might be potentially applied in the practical combustion atmosphere.

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