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Gas sniffer (YSZ-based electrochemical gas phase sensor) toward acetone detection

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ABSTRACT

Acetone sniffer, because of its ability of continuous non-invasive monitoring, is recognized as a potential method for the diagnosis of diabetes. In this study, mixed potential electrochemical sensors based on YSZ and K_2NiF_4 -type oxides $Sm_{2-x}Sr_xNiO_4$ (x = 0.4, 0.6 and 0.8) sensing electrode were fabricated as bio-sniffer for diagnosis of diabetics by detecting acetone concentration in exhaled breath. The results showed that when $Sm_{1.4}Sr_{0.6}NiO_4$ was used as sensing material, the fabricated sensor exhibited the best performance in comparison with other sensors, the present device also exhibited prominent reliability, excellent humidity resistance and good stability over 30 days. What's more, the low detection limit of sensor to acetone was 300 ppb, indicating that the sensor had ability for acetone detection in exhaled breath. The exhaled breathes of the diabetics with ketosis were used for detection and results showed that the sensor had a manifest and stable signal. Besides, the response and recovery time were also acceptable to real-time detection. In addition, the relationship of the blood ketone level and the acetone concentration in exhaled breath was given in the paper. Above all, the fabricated sensor has enormous potentiality for the diabetes monitoring through breath analysis.

1. Introduction

In the past ten years, with the improvement of people's living standards, aging population and lifestyle changes, the number of diabetics demonstrated a rapid growing trend, diabetes has been a major health threat and social threat to humanity and attracted worldwide attention [1,2]. At present, the diagnosis of diabetes is depended on blood analysis, which might bring pain to the patient and have a certain probability of infecting illness [3]. According to the Pathologic surveys and studies [4–6], when the body is sick, the metabolite in human body is changed and enters the bloodstream, causing the change in the content of blood metabolites, which enter the lungs through the blood barrier and exhale out of the body, leading the change of some specific gas concentration in human breath [7–10]. Breath analysis, owing to the similarity with blood analysis and non-invasion, has high application prospect and research significance in disease diagnosis, human metabolism monitoring and drug developing, especially in diabetes diagnosis [11–13]. In ordinary circumstances, human blood contains a small amount of ketone bodies (0.03–0.5 mmol/L), however, for diabetes patients with ketosis, due to fat metabolism worsens, the concentration of ketone in blood would increase [14]. Blaikie et al. [15] had investigated that the amount of acetone in human breath and blood ketone concentration performed a strong positive correlation, therefore the level of acetone in human breath was regarded as an important biomarker to reflect the ketone body level in blood. According to the literature, the concentration of acetone in healthy human breath was 0.3–1 ppm, however in diabetics breath is 1–20 ppm or even higher [16,17]. Hence, it is useful to monitor blood ketone levels of human through non-invasive blood test methods for the prevention and early diagnosis of diabetes. If selective acetone sensing could be performed at the sub-ppm level, noninvasive diabetes monitoring through breath analysis would become possible [18–20].

Human breath contains thousands of VOCs [21], complicated component and low in concentration. Hence, the detecting technique for the analysis of one gas component should have high sensitivity and selectivity, furthermore, the response and recovery time is also an important parameter in POCT (point of care testing). Recently, the detection of low concentration gas depends on gas chromatography/mass spectroscopy (GC/MS) and differential mobility spectroscopy (DMS) [22], which is not suitable in diabetes diagnosis because of large size,

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high price and disability to real-time detection. Owing to low price, simple fabrication, real-time diagnosis, gas sensor has been considered as a simple and effective approach for acetone detection and became one of the most written topics [23–27]. In various gas sensors, YSZ-based mixed potential electrochemical gas sensor, because of its high sensitivity, low detection limit and good stability, has been widely investigated. Lately, according to the literature [28–34], the performance of mixed potential type gas sensors was closely related to the sensing material, and most researchers focused on the type of sensing material and whether single oxides or complex oxides were investigated to fabricate YSZ-based sensor for acetone detection [35,36], which performed some surprising properties, however, it is also a challenge to fabricate the YSZ-based sensor with low detection limit and good selectivity.

As a type of function material, K_2NiF_4 -type oxides have been investigated and used in many electrochemical fields. According to the previous reports, researchers successfully used Sr to replace a part of Sm to compound a new type complex oxide $Sm_{2-x}Sr_xNiO_4$, which performed good properties in the solid oxide fuel cell field [37]. However, there was few literature about using $Sm_{2-x}Sr_xNiO_4$ as sensing electrode to fabricate YSZ-based mixed potential type sensor. Consequently, in this paper, a type of K_2NiF_4 -type oxides $Sm_{2-x}Sr_xNiO_4$ was synthesized to fabricate the YSZ-based mixed potential gas sensor, and the samples of diabetics out-breath were collected for the clinical detection using the sensor we fabricated.

2. Experimental

2.1. Preparation and characterization of $Sm_{1-x}Sr_xNiO_4$ sensing electrode material

The $Sm_{2-x}Sr_xNiO_4$ (x = 0.4, 0.6 and 0.8) were prepared by a simple sol-gel method. Samarium nitrate hexahydrate ($Sm(NO_3)_3{\cdot}6H_2O$), strontium nitrate ($Sr(NO_3)_2$), nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$) and citric acid (CA) were purchased from Sinopharm Chemical Reagent Co., Ltd and used as raw materials, besides, all of materials were of analytic grade without further purification. The synthetic process of the sensing materials was as following.

Initial reagents samarium nitrate, strontium nitrate and nickel nitrate in their stoichiometric ratios were dissolved in the double distilled deionized water, separately. The strontium nitrate solution and nickel nitrate solution were dropped wise into the samarium nitrate solution, and the mixed solution was stirring in the water bath at 60 °C to form precursor solution. Citric acid with the mole proportion of citric acid and total metal iron ($n(Sm^{3+} + Ni^{2+} + Sr^{2+})$) = 1:1 was dropped into the mixed solution. And the resultant solution was stirred at 80 °C for two hours until a gel was obtained. Then, the obtained gel was maintained at 80 °C for 48 h at a vacuum drying oven. Finally, the precursor gel was introduced into a muffle furnace and sintered at 1000 °C for 5 h to get target products.

The structure and phase stability of the materials were characterized by X-ray powder diffraction on a Rigaku wide-angle X-ray diffractometer (D/max rA, using Cu Kα radiation at wave length = 0.1541 nm) in the angular range of 2θ = 20-80°. The morphology and micro-structure of the sintered electrodes were examined with Hitachi JSM-7500 F FEG-SEM operating at 15 kV.

2.2. Fabrication and measurement of gas sensor

The sensor was manufactured utilizing YSZ plate (8 mol% Y_2O_3-doped, 2 mm × 2 mm square, 0.3 mm thickness, provided by Anpeisheng Corp. China). The relative description in the supporting information and the detailed structure of the sensor we fabricated was shown in our previous work [38]. The Pt heater provided enough heat in order to satisfy the right temperature to the sensors with a linear DC Power Supply (Gwinstek GPD-3303S), The gas sensing performance of the gas sensors were investigated using a digital electrometer (Rigol Technologies, Inc, DM3058, China). The complex impedance of the sensor in sample gas was measured by means of an impedance analyzer (Solartron, 1260 and Solartron, 1287) in the frequency range of 0.1 Hz-1 M Hz. The obtained results were recorded with a computer connected to the electrometer. When exposed to air or sample gas, it has a series of voltage signals because of the difference of the electric potential between the SE and RE of the sensor, The response of the sensor (ΔV) was given by ΔV = Vacetone-Vair, and the time of the sensor exposed to the sample gas containing different acetone concentration was approximately same, in this case, Vacetone denote the figure of the last second in the sample gas and Vair denote the figure of the last second in the air. The exhaled human breathes in this work were offered by The Second Hospital of Jilin University and all experiments presented in this work were performed in compliance with the relevant laws and institutional guidelines of China. The sample gas of every volunteers was collected into a gas-collecting bag. Before measurement, an airtight chamber with volume of 1 L was pumped into vacuum pressure, then, the sample gas was pressurized into chamber by difference pressure, finally the sensor fabricated was placed in the airtight chamber.

3. Result and discussion

The crystallographic structure of the sensing materials $Sm_{2-x}Sr_xNiO_4$ was characterized by X-ray powder diffraction (XRD) analysis, the results and related discussion exhibited in support information identifies that the materials we compounded was the oxides of K_2NiF_4-type structure. In addition, the micro-structure of the sensing materials $Sm_{2-x}Sr_xNiO_4$ was investigated by FESEM and the SEM images are shown in support information. The sensing materials have been reunited because of high sintered temperature of 1000 °C, causing the sensing material to perform a porous structure, which is important for the sensing performance of the sensor. According to the early work by Co-workers [39,40], the sensing characteristics of the present devices abide by the mixed-potential theory and it has the following electrochemical reactions for the sensor.

In air: O_2, $Sm_{2-x}Sr_xNiO_4$ / YSZ / Pt, O_2

In sample gas: $C_3H_6O + O_2$, $Sm_{2-x}Sr_xNiO_4$ / YSZ / Pt, $C_3H_6O + O_2$

The reaction (1) occurred at the process that sample gas went through the electrode layer, which caused a portion of consumption and decreased the gas concentration arriving at the TPB (triple phase boundary, the interface of $Sm_{1-x}Sr_xNiO_4$-SE, acetone and YSZ), hence, the sensing material should be porous in order to accelerate diffusion speed and decrease the consumption. The electrochemical cathodic (2) and (3) reactions took place at TPB at the same time and a local cell was formed at SE when the sensor under the acetone gas atmosphere. Till the electrochemical reactions occurred at the same rate, a dynamic equilibrium reached, and the electrode potential in this time is called the mixed potential. The potential difference between the sensing electrode and reference electrode is required and regarded as the sensing signal.

$$C_3H_6O + 4O_2 \rightarrow 3CO_2 + 3H_2O \quad (1)$$

$$4O_2 + 16e^- \rightarrow 8O^{2-} \quad (2)$$

$$C_3H_6O + 8O^{2-} \rightarrow 3CO_2 + 3H_2O + 16e^- \quad (3)$$

Fig. 1(a) shows the response of the sensor based on $Sm_{2-x}Sr_xNiO_4$-SE. It was obviously seen that all of the sensors had a clear response to 5 ppm acetone, furthermore, the sensor based on $Sm_{1.4}Sr_{0.6}NiO_4$-SE had the largest response of −21 mV to 5 ppm acetone in comparison to the sensors based on other materials. In order to explain the difference of sensing responses of the sensor based on $Sm_{2-x}Sr_xNiO_4$-SE, we put the sensors into the sample gas of N_2 and 5 ppm acetone, in this case,

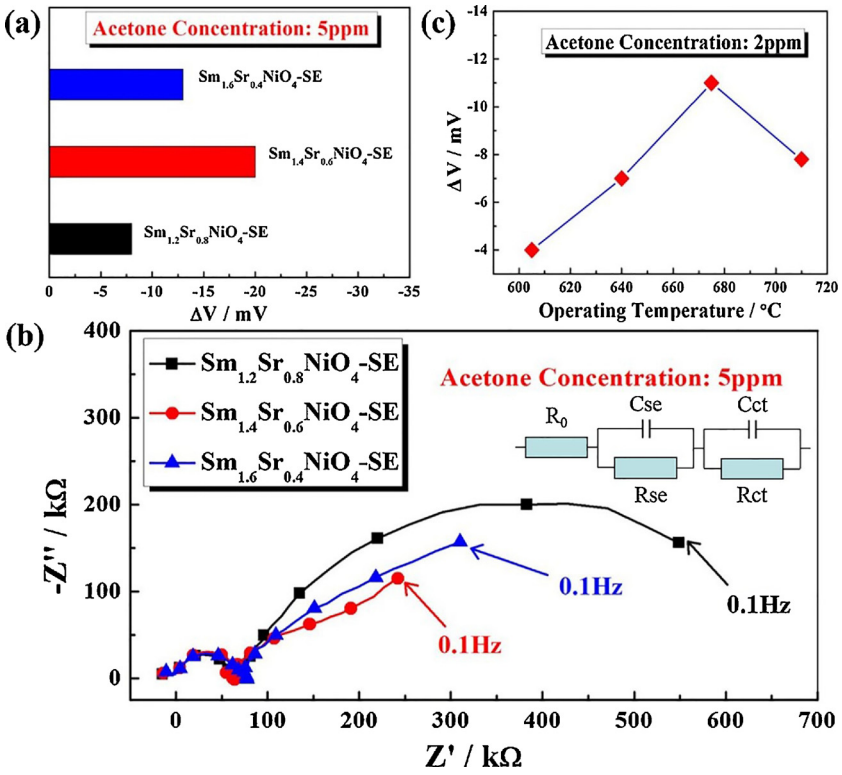


Fig. 1. (a) The response for the sensors based on $Sm_{2-x}Sr_xNiO_4$ (x = 0.4, 0.6 and 0.8)-SEs to 5 ppm acetone. (b) Complex impedance curves in 5 ppm acetone for the sensors attached with $Sm_{2-x}Sr_xNiO_4$ (x = 0.4, 0.6 and 0.8)-SEs. (c) The response of sensor attached with $Sm_{1.4}Sr_{0.6}NiO_4$-SE to 2 ppm acetone at different operating temperatures.

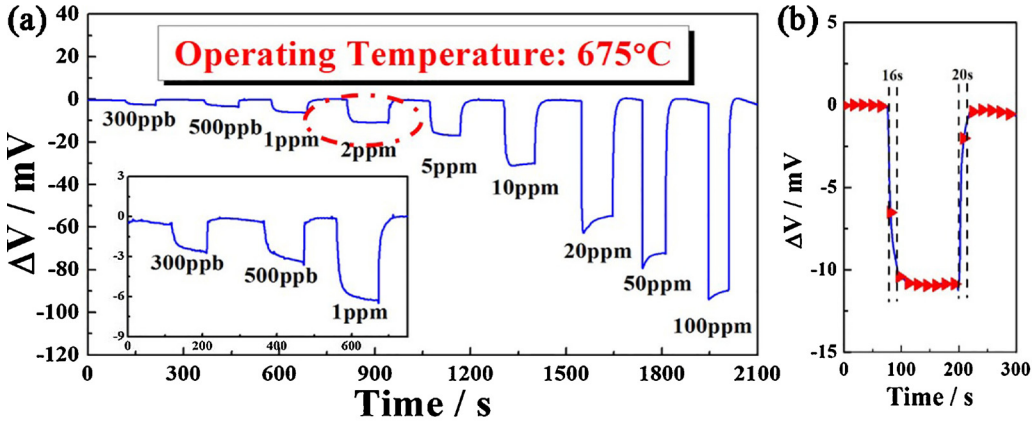
Table 1
Ohmic resistance and interfacial resistance of the sensors based on $Sm_{2-x}Sr_xNiO_4$ (x = 0.4, 0.6 and 0.8)-SEs to 5 ppm acetone at 675 °C.

Sensing Electrode	Ohmic Resistance (kΩ)	Interfacial Resistance (kΩ)
$Sm_{1.6}Sr_{0.4}NiO_4$	97	472
$Sm_{1.4}Sr_{0.6}NiO_4$	97	390
$Sm_{1.2}Sr_{0.8}NiO_4$	98	502

without oxygen, the reaction (1) rarely occur, hence we can compare the effects of reaction (1) and reaction (2, 3) on the sensing property of the sensor by comparing the response of the sensor to 5 ppm acetone and a mixture of nitrogen and air [41]. The responses of the sensor based on $Sm_{2-x}Sr_xNiO_4$ (x = 0.4, 0.6 and 0.8)-SEs to the sample gas of N_2 and 5 ppm acetone could be seen in Fig S3, we named the response of the sensor to the sample gas of N_2 and air were V_N and V_{air}, respectively, all the responses of the sensor based on $Sm_{2-x}Sr_xNiO_4$ (x = 0.4, 0.6 and 0.8)-SEs had increased, however, the degrees of improvement were about nearly same, the radio between the response of ΔV (V_N-V_{air}) and V_{air} were 33%, 35% and 30%, respectively, which indicated that the influence of the reduction to reaction might not a main parameter at 675 °C. We considered that the improvement of the response was mainly depended on the enhanced electrochemical activity at the TPB, therefore the complex impedance was investigated and result is shown in Fig. 1(b). The appropriate equivalent circuit was also shown in Fig. 1(b), the Ohmic resistance and interfacial resistance was also shown in Table 1. According to the reported literature [42,43], The intercept of the high frequency arc with the real axis corresponds to the ohmic resistance of the device, and that of the low frequency represents the total resistance, The difference between ohmic resistance and total resistance is the resistance of the interface between the electrolyte and electrode. The ohmic resistance of the device, which based on the intrinsic property, had almost no change at a steady temperature, the interfacial resistance represents the strength of the electrochemical reaction, which are typically related to mass transport processes such as gas diffusion and adsorption. Miura et al. reported that the sensitivity of sensor might be attributable to the change in the resistance of electrochemical reaction between the interface of YSZ/oxide SE and sample gas at a high temperature. Obviously, the interfacial resistance of the sensor based on $Sm_{1.4}Sr_{0.6}NiO_4$-SE was decreased compared with other sensors at the lower frequency range, Table 1 shows the accurate interfacial resistances of the sensors based on $Sm_{2-x}Sr_xNiO_4$-SE. Changes in the interface resistance measured in different sensors mean the ability of electrochemical catalytic activity and the result revealed that $Sm_{1.4}Sr_{0.6}NiO_4$-SE performs the highest electrochemical catalytic activity [43], which was conformed to the sensing properties of the sensor based on $Sm_{2-x}Sr_xNiO_4$-SE performed. Consequently, the sensor attached with $Sm_{1.4}Sr_{0.6}NiO_4$-SE has highest sensitivity to acetone in comparison with other sensors.

The optimum operating temperature, viewed as a necessary parameter, was investigated as seen in Fig. 1(c), the response and recovery transients of the sensor to 2 ppm in different operating temperatures (605 °C, 640 °C 675 °C and 710 °C) were clearly exhibited and it was obvious that the response to 2 ppm acetone at the operating temperature of 675 °C was highest in comparison with that at other operating temperatures. Moreover, it should be noted that the response to 2 ppm acetone shifted upward as the operating temperature increased from 605 °C to 675 °C, but shifted downward suddenly above 710 °C. The reason of this phenomenon had been interpreted in our previous work [44]. Hence, the optimal working temperature was ensured to be 675 °C and the sensing performances were investigated mainly at present temperature in the next work.

The response and recovery property of the sensor based on $Sm_{1.4}Sr_{0.6}NiO_4$-SE to different acetone concentration was shown in Fig. 2(a). It was surprising that the low detection limit of the sensor was 300 ppb and the response value was -1.8 mV, which displayed the ability of low concentration acetone detection and performed the potential to detect diabetes. In addition, for the purpose of intuitively showing the response and recovery property, the response and recovery transient to 2 ppm acetone was separate and exhibited in Fig. 2(b), it was clearly seen that the typical 90% response was 16 s and the recovery time was approximately 20 s, which is acceptable for a



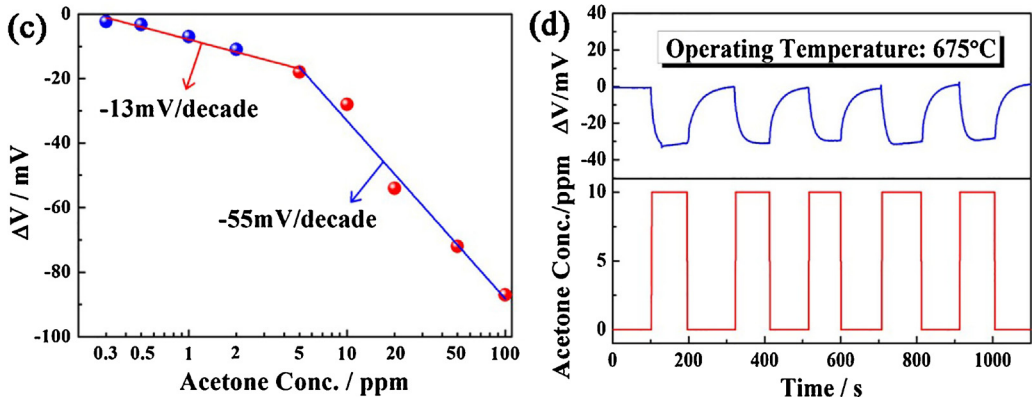


Fig. 2. (a) Response and recovery transient curves for the sensor attached with $Sm_{1.4}Sr_{0.6}NiO_4$-SE to different concentrations of acetone in the range of 0.3–100 ppm at 675 °C. (b) The response and recovery transient curves of sensor to 2 ppm acetone. (c) Dependence of ΔV for the sensor attached with $Sm_{1.4}Sr_{0.6}NiO_4$-SE on logarithm of acetone concentration in the range of 0.3–100 ppm at 675 °C. (d) Continuous response-recovery transient curves to 10 ppm acetone for the sensor using $Sm_{1.4}Sr_{0.6}NiO_4$-SE at 675 °C.

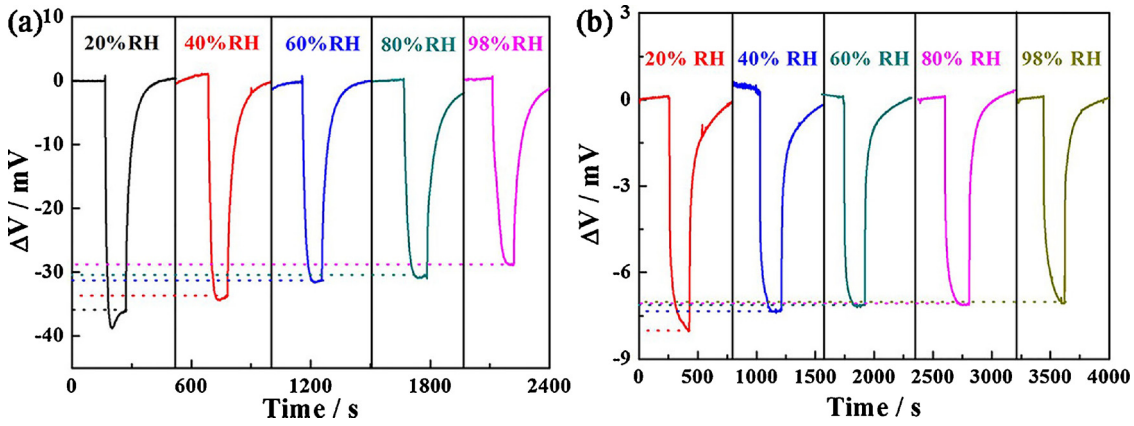


Fig. 3. Response and recovery transients for the sensor using $Sm_{1.4}Sr_{0.6}NiO_4$-SE annealed at to (a) 10 ppm acetone and (b) 1 ppm acetone under 20%, 40%, 60%, 80% and 98% RH at 675 °C.

successful sensor. Moreover, Fig. 2(c) shows the dependence of ΔV on the logarithm of corresponding acetone concentration for the sensor at 675 °C. As the results exhibited, ΔV and the logarithm of acetone concentration in the examined range of 0.3–100 ppm performed a linear relationship, which conformed to the mixed potential theory [45–48]. The slope of the sensor acetone was −13 mV/decade in the examined range of 0.3–5 ppm and-55 mV/decade in the examined range of 5–100 ppm, which was considered as sensitivity. The reasons of this phenomenon were depended on the energy of the electrochemical and the diffusion process, which was investigated carefully in our early studies [44]. The relationship of ΔV and the logarithm of acetone concentration might be described as followed equation (Eq. 1):

$$\Delta V = -13\lg C - 7.9 (0.3ppm < C < 5ppm)$$
$$\Delta V = -55\lg C + 21 (5ppm < C < 100ppm)$$

Fig. 2(d) shows the continuous response and recovery characteristic of the sensor to 10 ppm acetone. As can be seen, the response value of the present device performed little fluctuation and the highest and lowest change errors of continuous responses, respectively, this result indicated that the sensor we fabricated could work continuously.

Human breath contains the number of water vapor, which might cause a great influence on the sensitivity of the sensor. Thus, the responses for the sensor attached with $Sm_{1.4}Sr_{0.6}NiO_4$-SE to 10 ppm and 1 ppm acetone in the relative humidity (RH) range of 20–98% at 675 °C were measured as shown in Fig. 3(a), the change amplitudes of the response for the sensor were about -12% to 9%–10 ppm acetone, and -10% to 8% to 1 ppm acetone, indicating that the impact of RH on the responses for the sensor was so tiny that can be ignored, the sensor we fabricated showed good humidity resistance both at high acetone concentration and at low acetone concentration. It was widely known that human breath contains a lot of ingredient, such as methanal, methanol, ethanol, CO_2, and so on which can disturb the sensor we

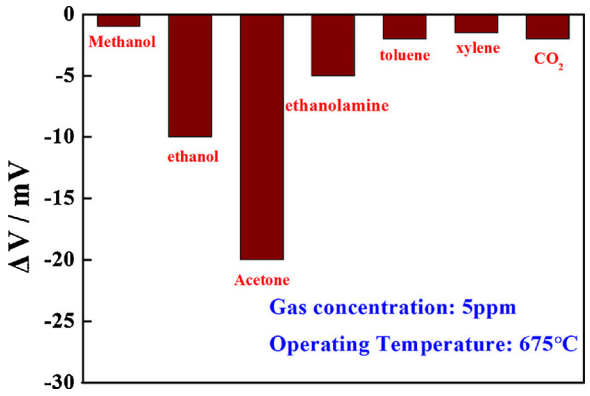


Fig. 4. (a) The responses for the sensor based on $Sm_{1.4}Sr_{0.6}NiO_4$-SE to 5 ppm various gases at 675 °C.

fabricated to make it out of work, therefore, the selectivity was one of the most important sensing properties for the sensor, and Fig. 4(b) shows the response signals for the sensor attached with $Sm_{1.4}Sr_{0.6}NiO_4$-SE to a series of interfering gases at 675 °C. The sensor displayed the highest response signal to 5 ppm acetone compared with the other gases.

Moreover, the stability of the sensor attaching with $Sm_{1.4}Sr_{0.6}NiO_4$-SE was explored by continuous test at 675 °C during 40 days. The response of the sensor to 2 ppm acetone was tested every day and the consequence is exhibited in Fig. 5(a) and (b). The change of the ΔV (ΔV_s) to the sensor was in the form of $\Delta Vs = [(\Delta V_n - \Delta V_0)]/\Delta V_0 \times 100\%$, the meanings of ΔV_n and ΔV_0 respectively were the response values of the sensor on the n and initial day, respectively. The changes of response value for the present sensor to 2 ppm acetone was about -9.1% on the 30th day. In addition, the response and recovery curve for the present device to 2 ppm acetone on the initial, 10th, 20th, and 30th days shown in Fig. 5(a) also further demonstrated the good stability. In conclusion, the device we fabricated could be used in a complex environment to work for a long time.

According to the above sensing analysis, clinical detection was applied to test the sensing performance of the sensor we fabricated in human breath. For detection, 6 diabetics and 1 healthy people participated in the test. The blood ketone concentrations tested from the second hospital of Jilin University were collected and listed in Table. 2. As can be seen, the response and recovery transient exhibited in Fig. 6 shows that the sensor had conspicuous and stabilized signals to the exhaled breathes of all volunteers. The sensor also performed fast response and recovery properties to every tests, which was acceptable for real-time detection, Furthermore, with the increase of the blood ketone concentration, the response had an evident increase as shown in Fig. 6,

Table 2
Comparison of the observed mixed potential and the estimated acetone concentration for the sensors attached with $Sm_{1.4}Sr_{0.6}NiO_4$-SE to the exhaled breath diabetics with different blood ketone levels.

Blood ketone. Conc (mmol/L)	Mixed potential (observed) (mV)	Acetone. Conc (estimated) (ppm)
0.3	−7	0.85
0.4	−9.8	1.45
0.8	−14	2.94
1.7	−20	5.56
1.9	−22	5.80
7.1	−30	8.46

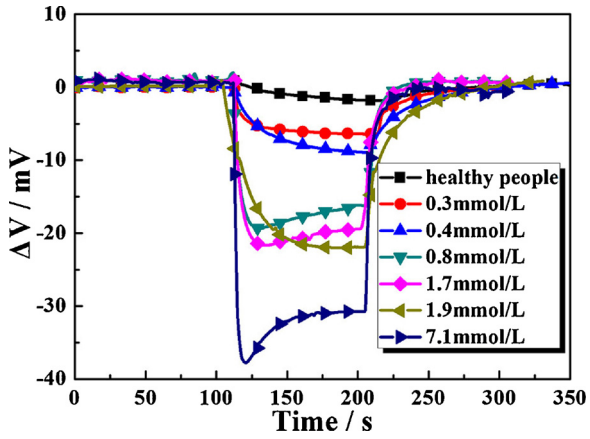


Fig. 6. The response and recovery transient curves of sensor to the volunteer of different blood ketone levels.

the dependence of ΔV on the corresponding blood ketone concentration was exhibited in Fig. 7(a). It is apparently seen that the response had a good positive correlation to the blood ketone levels, the concentration of the acetone could be approximately assumed by Eq. (1) and Fig.7(b) exhibited that the acetone concentration also had a positive correlation to the blood ketone level, which was in good agreement with the experimental results shown in other recent reports. (The detailed statistics were listed in Table 2).

Among the literature recently published [49], the critical concentration of blood ketone is 0.4 mmol/L, when the blood ketone of one person was above this level, He or she would have a high probability of developing diabetes with ketosis. Thus, we have also gathered 3 exhaled breathes of the diabetics with the ketone concentration of 0.4 mmol/L for detection, the volunteers were abbreviated to V1, V2 and V3 respectively, and the result was exhibited in Fig. 8. The sensor

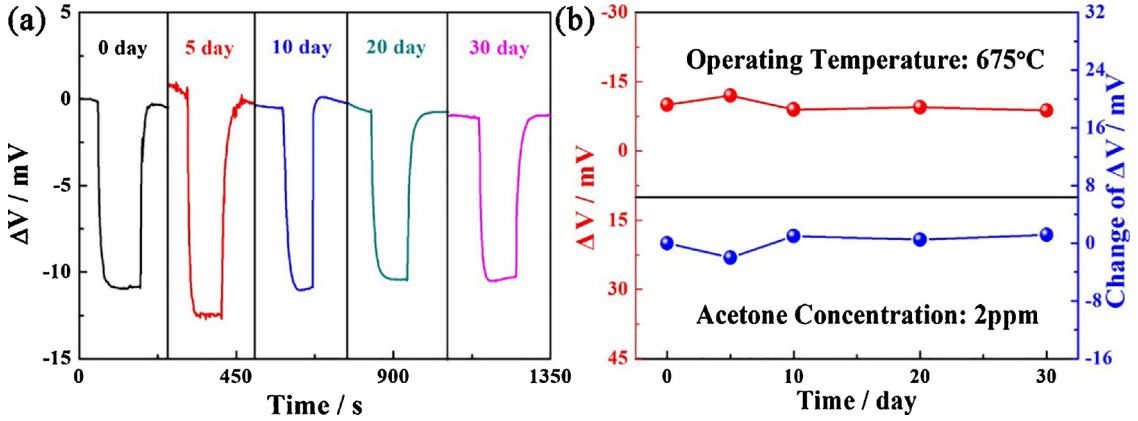


Fig. 5. (a) Long-term stability for the sensor attached with $Sm_{1.4}Sr_{0.6}NiO_4$-SE to 2 ppm acetone. (b) Response and recovery transients for the sensor $Sm_{1.4}Sr_{0.6}NiO_4$-SE at 675 °C to 2 ppm acetone on the initial, 10th, 20th and 30th days at 675 °C.

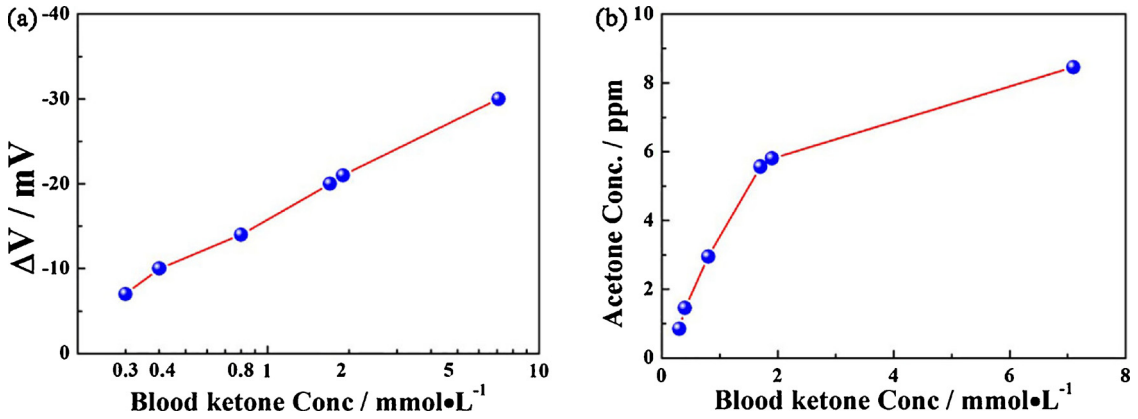


Fig. 7. (a) Dependence of ΔV for the sensor attached with $Sm_{1.4}Sr_{0.6}NiO_4$-SE on blood ketone concentration. (b) Dependence of acetone concentration on the blood ketone concentration though the test by the sensor we fabricated.

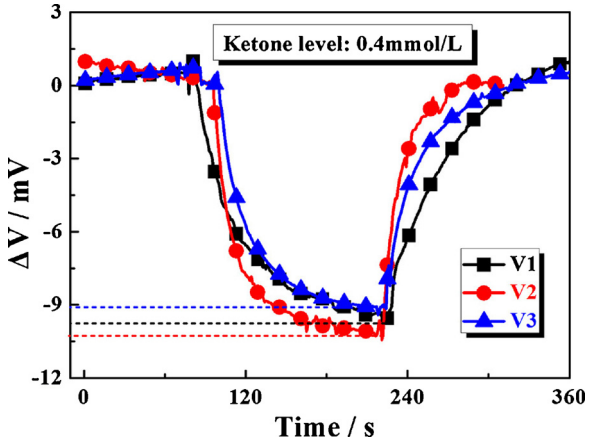


Fig. 8. Three response and recovery transient curves of sensor to three volunteers, the ketone concentrations of every volunteer were as same as 0.4 mmol/L.

we fabricated performed stabilized response and recovery properties to every exhaled breathes, the values of the responses were −10 mV, −9.8 mV and −9.5 mV respectively, obviously higher than that to healthy people (−2 mV) (shown in Fig. 6). Hence, the sensor we fabricated has ability to distinguish the diabetic with ketosis from healthy person. In conclusion, the present device performed stabilized and credible properties in clinical detection, which indicated that the sensor we fabricated performs ability to detect the diabetes with ketosis and has great potentiality for the diabetes monitoring through breath analysis.

4. Conclusion

In summary, YSZ-based mixed potential gas sensor with $Sm_{2-x}Sr_xNiO_4$ (x = 0.4, 0.6, and 0.8)-SEs synthesized by sol-gel method was fabricated and used as a bio-sniffer for detection of acetone at 675 °C. The sensor attached with $Sm_{1.4}Sr_{0.6}NiO_4$-SE exhibited the largest response to acetone in 5 ppm concentration at 675 °C in comparison to those of using other sensing electrode materials. The present sensor also shows the low detection limit of 300 ppb to acetone, which had a faithful value of −1.8 mV. Moreover, the present device also displayed good repeatability, selectivity, humidity resistance, and stability in 30 days work. What's more, the human breathes of healthy people and diabetics with ketosis were gathered for the detection and the result shows that the sensor we fabricated has evident and stabilized response signal to exhaled breathes of every volunteers, whether healthy people or diabetics with different ketone concentrations. Therefore, according to the acceptable acetone sensing properties, the present fabricated sensor is considered as a candidate in the aspect of monitoring acetone and has great potentiality for the diabetes monitoring through breath analysis.

Acknowledgements

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.snb.2018.09.025.

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