



Original Article

Feasibility study of a resistive-type sodium aerosol detector with ZnO nanowires for sodium-cooled fast reactors

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ABSTRACT

In sodium systems, leakage is one of the safety concerns; it can cause chemical reactions, which may result in fires. There are contact and non-contact types of leak detectors, and the conventional method of non-contact type detection is by gas sampling. Because of the complexity of this method, there has always been a need for a simple gas sensor, and the resistive-type nanostructure ZnO sensor is a promising option with various advantages. In this study, a ZnO sensor was fabricated, and the concept was tested as a leak detector using a dedicated experiment facility. The experiment results showed distinctive changes in resistance with the presence of sodium aerosol under various conditions. Replacing the conventional gas sampling with the ZnO sensors is expected to enable identification of the leakage location if used as a point-wise instrumentation and to greatly reduce the total cost, making the system simple, light, and effective. For further study, more tests will be performed to evaluate the sensitivity of key parameters under various conditions.

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1. Introduction

Sodium, the sixth most abundant element on earth, has excellent thermal properties and is compatible with various commonly used structural materials. However, sodium leakages may result in fires due to the reaction of the leaked sodium with oxygen and moisture in the atmosphere. Because of the high chemical reactivity of alkali metals with moisture, hydrogen can be generated by chemical reactions, resulting in explosions with reaction heat [1–3]. Despite these potential hazards, the high boiling point of sodium allows systems to operate under nearly atmospheric pressure conditions [4–6]. A good example of such a system is the sodium-cooled fast reactor, which is designed to operate at atmospheric pressure. Under this condition, there is no abrupt leakage of the coolant after the failure of the pressure boundary, and ‘sodium leak detection systems’ are the key to prevent and mitigate the consequences of leakages.

There are two different types of sodium leak detectors developed in the United State and Japan: the contact-type leak detector (CLD) and the sodium aerosol detector with a gas sampling process

that uses a sodium ionization detector (SID) or radioactive ionization detector (RID) [7–11]. The CLD detects the leakage only when in direct contact with the sodium; thus, the location of the leakage can be specified, but the detection time can be delayed, because sufficient amount of sodium must be accumulated to create a contact signal. On the other hand, the target in sodium aerosol detection is the reactant aerosol from the sodium-oxygen and/or sodium-moisture reaction. The detection response is relatively quick, and the detection time is quick because of the high sensitivity. However, the system is complicated due to the additionally installed components for gas sampling, such as blowers and flowmeters. Moreover, the separation between the leakage point and the detector inevitably makes it difficult to locate the exact point of the leakage. Therefore, a sodium aerosol detector as an individual sensor without gas sampling is essential at proper locations. It can also mitigate the limitation of existing leak detection systems and enhance their reliability.

Recently, many researchers have considered zinc oxide (ZnO) for various gas sensors, and the advantages of this method are a wide band gap of 3.37 eV, low cost, non-toxicity, high electron mobility, and thermal stability in high temperature conditions [12,13]. The gas sensor based on ZnO is generally used for detecting the reducing gas (i.e., ethanol); therefore, it can be used to detect

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sodium aerosols with a similar mechanism [13]. Previous studies on ZnO-based gas sensors mainly focused on the effect of the nano-scale structures or the doping of a specific element; however, there are no practical studies on sodium aerosols. In this study, a conceptual sodium aerosol detector using ZnO for an advanced sodium leak detection system is proposed and experimentally verified. This sensor device is small, simple, and effective. An experiment is designed to evaluate the performance of the resistive-type sensor with ZnO nanowires.

2. ZnO sensor design and fabrication

2.1. Detection mechanism

ZnO is characterized by high electron mobility and thermal stability at high temperatures. Consequently, many researchers have attempted using it for oxidizing/reducing gas sensors in a wide range of applications. The key parameter in sodium-aerosol detection is the change in electric resistance. Before the sodium leakage (Normal State in Fig. 1), the oxygen near the ZnO nano-structure exists as an ion due to the high electron mobility. However, after the sodium leakage (sodium environment in Fig. 1), there is a change in resistance (R) because of the reaction between oxygen ions and sodium vapor. The major chemical reactions are illustrated in Fig. 1. By monitoring the real-time resistance of the ZnO sensor, the real-time resistance value can be compared to that at the normal state. R_{ref} and R_{min} are the resistances of the gas sensor in air and in the sodium aerosol environment, respectively. The time taken for the resistance to change from R_{ref} to R_1 , $R_{ref} - 0.9(R_{ref} - R_{min})$, when the sensor is exposed to the sodium aerosol is defined as the response time.

2.2. Sensor design and fabrication

The sensor was fabricated to be as simple as possible to verify the concept. The ZnO seed layer was selectively deposited on the topside of the commercial interdigital electrode by magnetron sputtering, as shown in Fig. 2. More details about this electrode are

presented in Table 1. Subsequently, the nanowire was allowed to grow for 3 h at 90 °C using hydrothermal synthesis with a $\text{ZnNO}_3 \cdot 6\text{H}_2\text{O}$ + hexamethylenetetramine (HMT) solution. As a result, the uniform nanorod structures were grown on the whole substrate. A summary of the fabrication process of the sensor is presented in Fig. 2.

2.3. Preliminary test for prepared sensor

Before the main detection test for high-temperature sodium aerosol, a preliminary test was carried out to confirm whether there was a resistance change due to the reaction with ethanol, as reported in the literature [13]. Fig. 3(a) shows the test set-up for detecting the resistance change of the ZnO sensor by injecting ethanol, and Fig. 3(b) shows the results of the resistance change for different amounts of injected ethanol (i.e., 3 mL and 10 mL). Notably, the resistance of the sensor increases steadily before ethanol vapor is injected. This is because of the light entering into the oven where the ZnO sensor is located. Despite efforts to block this light, tiny amounts of incoming light reacted with the ZnO sensor, resulting in changes in the resistance. However, a decrease in the sensor resistance was observed when the valve was open to allow ethanol vapor in (Fig. 3(b)). When a larger amount of ethanol was injected, a significant and clear resistance drop was observed, which shows that the reaction of the ZnO sensor with ethanol vapor caused the resistance drop and that the concept works. The main experiment will be done under completely light-blocked condition and the resistance change will be observed in more distinguishable way.

3. Feasibility study on sodium leak detection

3.1. Experiment facility

To evaluate the feasibility of a ZnO sensor for sodium, an experiment facility was designed and implemented. It contains two high-temperature chambers: one is designed to generate sodium aerosol and the other for is testing the ZnO sensor detection. A gas

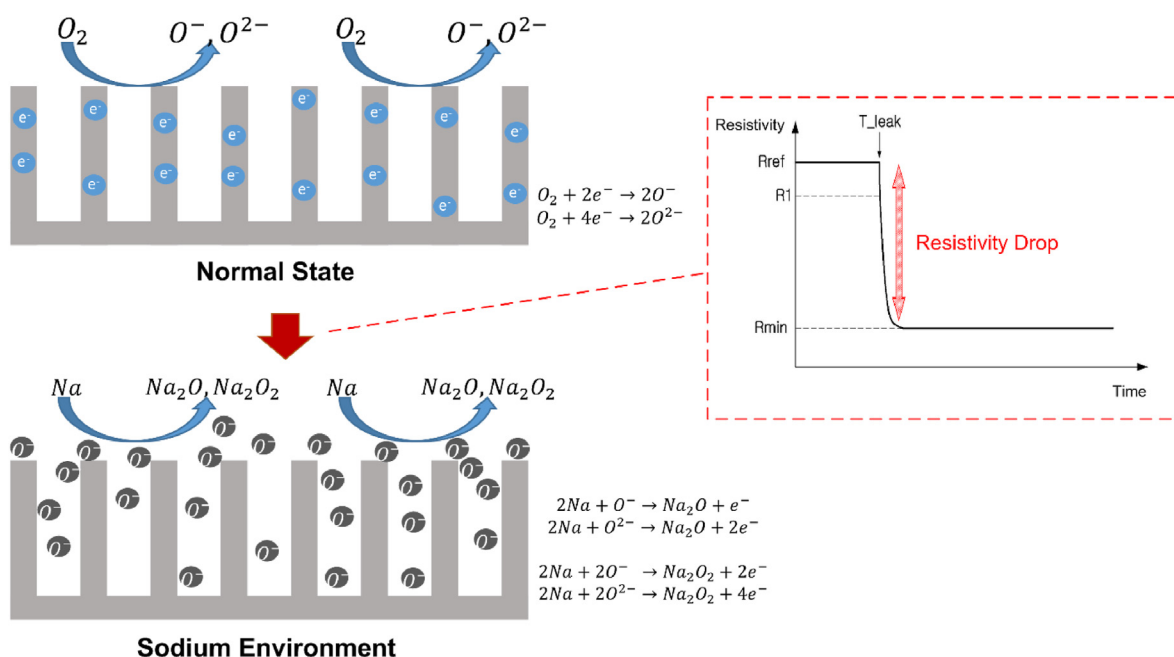


Fig. 1. Detection mechanism of sodium aerosol by a resistivity drop.

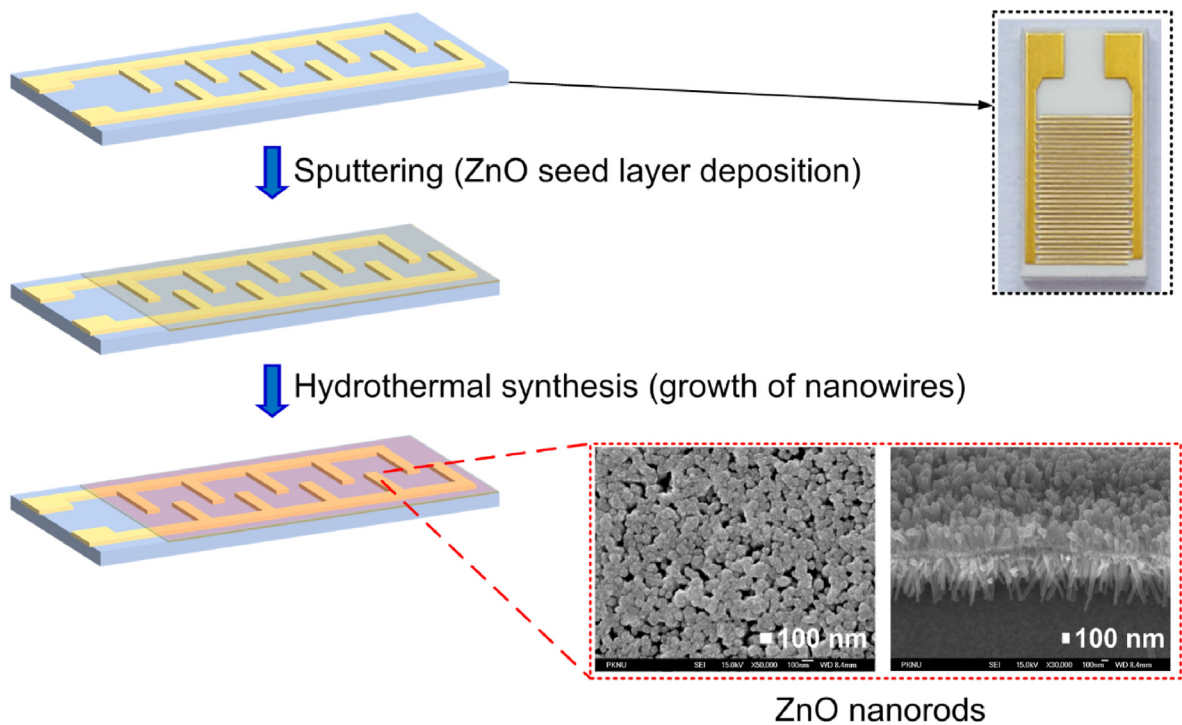


Fig. 2. Fabrication process of the sensor with ZnO nanorods on the surface.

Table 1

General specification of the interdigital electrode.

Overall size	5 × 10 (mm)
Line Width	100 (μm)
Line Space	100 (μm)
Number of Interdigital Pairs	15 (30 fingers)
Substrate	Alumina ceramic (thickness: 0.653 mm)
Conductive material	Gold (thickness: 5 μm)
Suitable Operating Temperature	−50–500 °C

mixture of O₂ and N₂ was supplied through individual gas lines, and Chamber 1 (where sodium vapor was generated by a sodium combustion furnace) and Chamber 2 (where the ZnO sensor was

installed and connected to measure the signal) were serially connected. The facility had a control panel, leak-detection source measure unit (SMU), and data acquisition system (DAQ). The details and layout of the facility are shown in Fig. 4. The sizes of Chambers 1 and 2 were the same, with a diameter of 200 mm and height of 150 mm. Both chambers had a pressure gauge and, vent valve on the side wall, and mold heater at the bottom surface to control the temperature. The design temperature and pressure of the system were 400 °C and 2 bar, respectively. There were three thermocouples (TCs) in vertical positions to control the bottom surface heater and measure the real-time space temperature. In addition, there was a bypass line for the bias stability test. The importance of sealing is emphasized due to the high temperature condition and

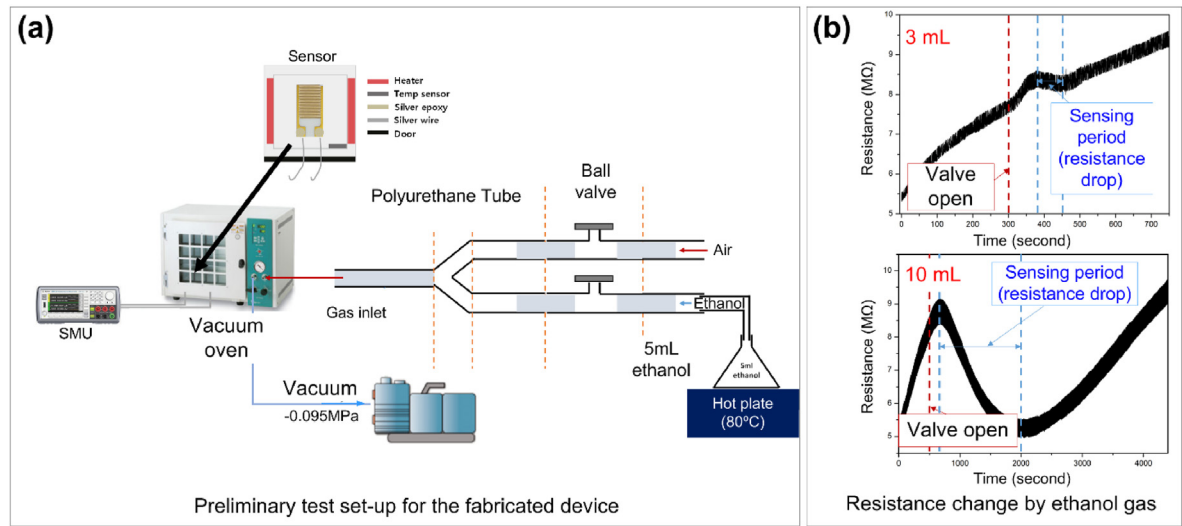


Fig. 3. Preliminary sensor test using ethanol gas: (a) set-up and (b) results of the resistance change.

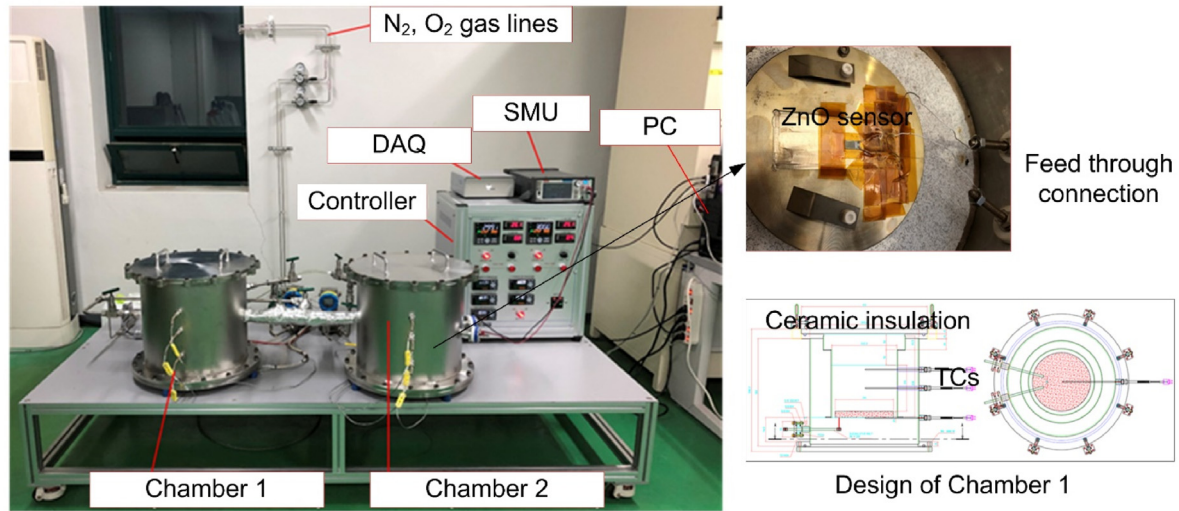


Fig. 4. Experiment facility of sodium leak detection test.

high sodium reactivity of this device compared to those of the ordinary devices. In this facility, complete sealing was successful after numerous tries and errors.

3.2. Experiment procedure

Chamber 1 generates sodium vapor or aerosol by reacting the high temperature liquid sodium with the mixed gas inflow from the gas supply. Chamber 2 receives the target gas from Chamber 1 to measure the electric signal of the ZnO sensor. Sodium aerosol detection starts with the application of an input voltage of 2.5 V by the SMU and measurement of the resistance in ohm. The concentration of the gas mixture is one of the important parameters and is controlled by the mass flow controller (MFC) of each gas within the range of 0.2–1 L/m. The focus is on the actual amount of oxygen to react with sodium; therefore, careful handling and accurate mixing are necessary.

All experiments were carried out in 4 steps, as shown in Fig. 5. First, the entire device is preheated while keeping Chambers 1 and 2 isolated to prevent a sudden temperature change when the gas is injected. Unexpected, abrupt temperature changes may affect the melting process of the sodium inside Chamber 1. Subsequently, the background signal of the ZnO sensor is stabilized under constant gas mixture ratio and flow rate conditions using the bypass line.

After the signal is sufficiently stabilized, the valve connecting Chambers 1 and 2 opens to expose the ZnO sensor to the sodium aerosol. Finally, Chamber 2 returns to the gas mixture environment without sodium aerosol using bypass line, and the resistance of the sensor is measured to check the recovery performance.

3.3. Experiment conditions

The main control parameters are the environment temperature and ratio of oxygen. Four cases were defined, as presented in Table 2. The oxygen ratio of the carrier gas mixture indicates the amount of sodium aerosol generated. The experiment was conducted using two cases (i.e., 10% and 15%). The average time required for a single experiment was approximately 5 d, and the temperature was maintained during the experiment by PID control. Because of this time-consuming characteristic, it was challenging to increase the number of cases for the experiment. Considering the trial-and-error process, the actual number of attempts to measure consisted of more than four cases.

3.4. Experiment result

The ZnO sensor was placed in Chamber 2, and after a sufficiently long time (approximately 2–3 days), the resistance value of the

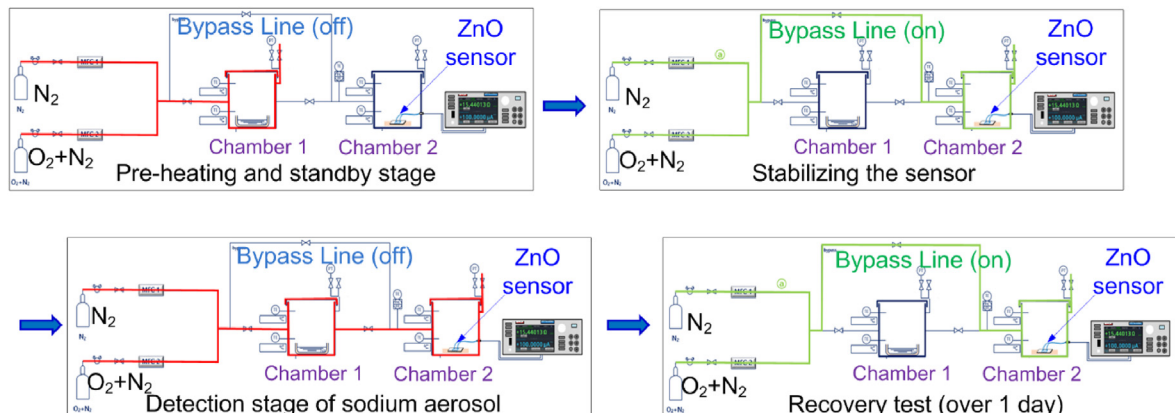


Fig. 5. Experiment procedure for sodium aerosol sensing.

Table 2
Conditions of the sodium aerosol sensing experiments.

Case	Temperature condition			Carrier gas condition		Input Voltage (SMU, V)
	Set Temp.(Heater, °C)	Measured Temp. (middle, °C)	Measured Temp. (high, °C)	Ratio of O ₂ (%)	Flow rate (L/min)	
A	200	125.7	124.2	15	2.0	2.5
B	250	164.0	161.3	15	2.0	
C	300	194.1	192.5	10	2.0	
D	350	230.2	226.0	10	2.0	

sensor stabilized, as shown in the beginning of Fig. 6. When the valve between Chambers 1 and 2 was opened while the bypass line was blocked, sodium aerosol was generated in Chamber 1 by the reaction between sodium and oxygen. Subsequently, the sodium aerosol moved to Chamber 2, and a sudden drop in resistance occurred, as can be seen in Fig. 6. After 1 h, the route between two chambers was blocked, and pure nitrogen gas was injected using the bypass line to dilute the sodium aerosol environment in Chamber 2. At this resistance recovery stage, the resistance stopped decreasing and started increasing again, as shown in Fig. 6. To prevent the ZnO sensor from being affected by the temperature change, the experiment conditions (flow rates, PID set values, heater power, etc.) were precisely controlled. In Fig. 6, the temperature is well maintained during the entire experiment, except for the temperature of the bypass line that is isolated from the sensor and does not affect the sensor.

The results of the experiment for the four cases are shown in Fig. 7. The resistance of the ZnO sensor dropped significantly due to the presence of sodium aerosol. The initial condition of stable resistance for each case differs depending on the condition of ZnO sensor fabrication; however, the abrupt reduction in resistance

after sodium aerosol injection was common. The quantitative analysis result of the resistance value measured in the experiment, denoted as R_1 and defined in previous section, and the time to reach this resistance, are presented in Table 3.

Notably, the time to reach R_1 was shorter as the temperature increased, although it is difficult to make a simple comparison among the four cases. In particular, the Case C and D showed similar R_{ref} and R_{min} values, whereas the response time of Case D was 18% smaller than that of Case C. This result implies that the ZnO sensor could possibly be applied to sodium reactors at temperatures higher than that in experiment. The general operating temperature range of sodium reactors is 200–550 °C.

4. Conclusion

The sodium leakage detection system is one of the most important parts for ensuring the safety of the reference system. Contact-type and non-contact type detectors are used in combination to supplement the limitations of each. The non-contact type detector is usually considered in the gas sampling method, which consists of a very complicated and large system, making it costly.

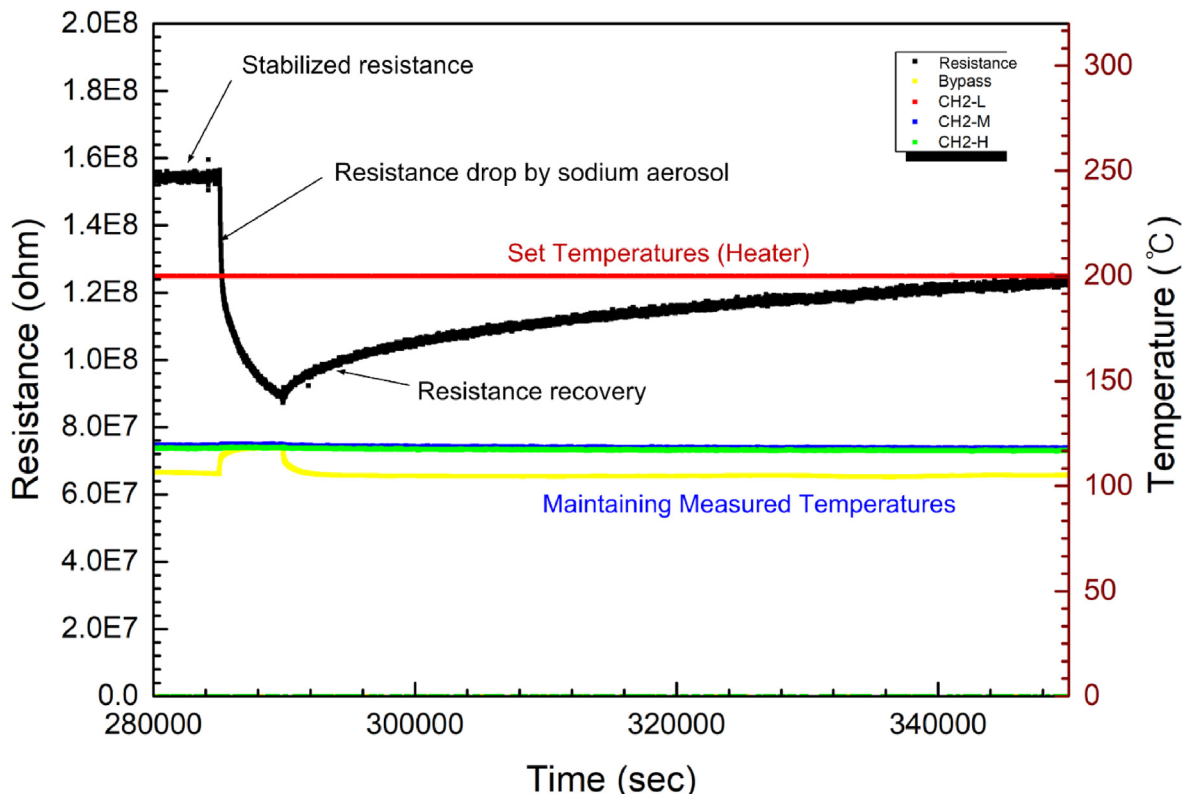


Fig. 6. Temperatures and resistance trends in the experiment (Case A).

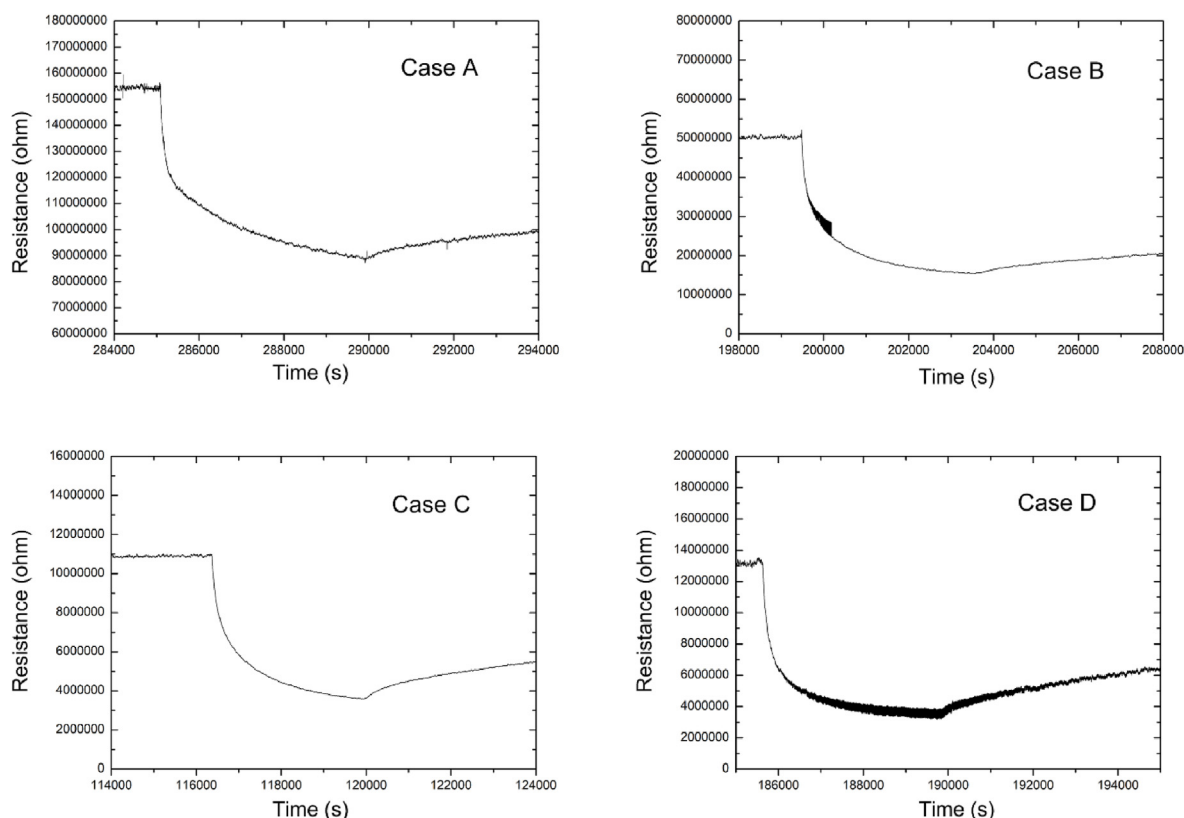


Fig. 7. ZnO sensor experiment results of four cases.

Table 3

Experiment results of the ZnO sensor using sodium aerosol.

Measured value	Case A	Case B	Case C	Case D
R_{ref} (ohm)	1.543E+08	5.022E+07	1.090E+07	1.313E+07
R_{min} (ohm)	8.861E+07	1.568E+07	3.604E+06	3.515E+06
R_1 (ohm) = $R_{ref} - 0.9(R_{ref} - R_{min})$	9.518E+07	1.913E+07	4.334E+06	4.477E+06
Response time (s, from R_{ref} to R_1)	2923	1711	1667	1369

There has always been a need for a simple, light, and effective gas sensor for sodium aerosol detection. The current research and effort on using a ZnO sensor for aerosol detection proved to be sufficiently effective for application. The main advantages are the wide band gap, low price, non-toxicity, high electron mobility, and thermal stability. By adopting the ZnO sensor for sodium aerosol detection, the complexity of conventional gas sampling can be greatly reduced, significantly lowering the cost. Moreover, by utilizing the ZnO sensor for point-wise detecting instrumentation, the location of the leakage can possibly be specified, contrast to conventional gas sampling. One of the suggestions to utilize as supplement and/or alternative to gas sampling is that placing the gas sensors at the point of concern in the system and using them as disposable one-time detector since they are very cheap and relatively easy to install. In this way, the overall safety feature will be enhanced in great manner.

In this study, to confirm the feasibility of detecting sodium leakage using a ZnO sensor, a dedicated experiment facility was designed and implemented to measure the resistance change by generating sodium aerosol. Owing to its natural characteristic of posing difficulties in multiple experiments, four cases were selected for testing. At least 300,000 s was required to obtain

meaningful data, and the results were collected for four different cases. Through the experiments, it was confirmed that a resistive-type ZnO sensor with nanostructures on the surface can effectively work as a leak detector for sodium aerosol in high-temperature environments. In the future, more tests are planned to analyze and evaluate the sensitivity of key parameters under various conditions.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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