Mixed-potential-type zirconia-based NO$_2$ sensor with high-performance three-phase boundary

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ARTICLE INFO

ABSTRACT

This paper focuses on the gas sensing properties of the mixed-potential-type NO$_2$ sensor based on yttria stabilized zirconia (YSZ) and NiO electrode. The sensing performance of the sensor was improved by modifying the three-phase boundary (TPB). Hydrofluoric acid with different concentrations (10%, 20% and 40%) was used to corrode YSZ substrate to obtain large superficial area of TPB. The scanning electron microscope and atomic force microscopic images showed that the 40% HF could form the largest superficial area at the same corroding time (3 h). The sensitivity of the sensor using the YSZ plate corroded with 40% hydrofluoric acid to 20–500 ppm NO$_2$ was 76 mV/decade at 850 °C, which was the largest among the examined HF concentrations. It was also seen that the sensor showed a good selectivity and speedy response kinetics to NO$_2$. On the basis of the measurements of anodic and cathodic polarization curves, as well as the complex impedance of the device, the sensing mechanism was confirmed to involve a mixed potential at the oxide sensing electrode.

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1. Introduction

Some of the most dangerous air pollutants, nitrogen monoxide (NO) and nitrogen dioxide (NO$_2$) (collectively referred as NO$_x$), have been of great concern in the past years due to their adverse health effects and abundance in the vicinity of roads, particularly in the high-density urban areas. Many toxicological and epidemiological studies established adverse health effects by NO$_x$ [1,2]. NO$_x$ can be produced in the process of the high temperature combustion of fossil fuels, so automotive vehicles as well as fuel hungry industries are the major sources of NO$_x$ emission [3–6]. Therefore, it is very important to control the emission of such gases and develop procedures for continuously monitoring these gases in the emission process and ambient atmosphere. In order to meet such needs, high performance NO$_x$ gas sensors are urgently demanded. So far, a special attention has been paid to the group of devices based on the mixed potential gas-sensing mechanism owing to their attractive performances [7–24]. In order to improve the sensing properties of mixed-potential-type NO$_2$ sensor, many researchers have been focused on the development of new oxide electrode materials and the optimization of the microstructure of these oxides. Miura et al. reported that ZnCr$_2$O$_4$, ZnFe$_2$O$_4$, NiO and Cr$_2$O$_3$ + NiO could give good sensing properties for NO$_x$ at elevated temperature [8–14]. Szabo and Dutta also examined that Cr$_2$O$_3$ was an excellent sens-

ing electrode [15]. Bartolomeo et al. testified that WO$_3$, LaFeO$_3$ and La$_{0.8}$Sr$_{0.2}$FeO$_3$ showed good sensing performance [16]. Xiong and Kale developed CuO + CuCr$_2$O$_4$ sensing electrode [17]. On the other hand, some researchers have been trying to optimize the microstructure of the oxide electrodes for increasing the sensitivity to NO$_x$. For example, Miura et al. investigated the dependence of the sensitivity on the thickness of NiO sensing electrode and found that the sensor exhibited the highest NO$_2$ sensitivity as well as fast response and recovery speeds at the operating temperatures below 800 °C when the thickness was about 120 nm [18,19]. Martin et al. used porous Cr$_2$O$_3$ as the sensing electrode material and found that the surface topography of sensing electrode affected the sensing performance of the sensor [20,21].

As stated above, at the initial stage of the investigation of the mixed potential sensors, most of the attentions were focused on searching for the new electrode materials. However, the effect of the microstructure of the three-phase boundary on the sensing performance was almost ignored. In some early researches, the flat YSZ plate or the YSZ tube with smooth surface were just covered with an electrode material layer, as shown in Fig. 1a. In this case, the effective area of three-phase boundary was decreased, which led to the decrease of the rates of electrochemical reactions. Miura et al. had investigated the relationship between the roughness of YSZ surface and the sensing property tentatively [22]. However, only simply contrastive research was carried out for commercially available YSZ plates with different surface roughness in their works, and the design and control of the surface roughness were not included.

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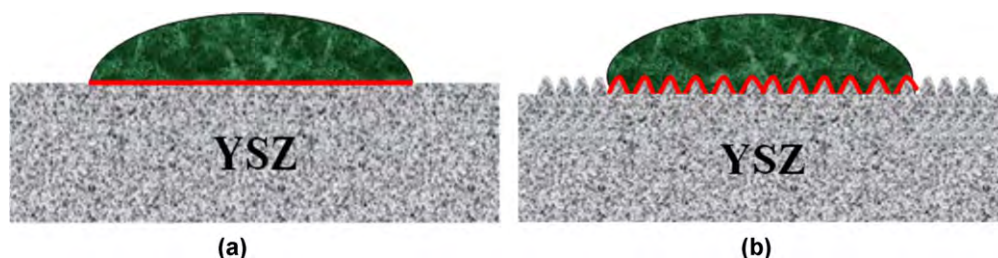*E-mail address:* lugy@jlu.edu.cn (G. Lu).

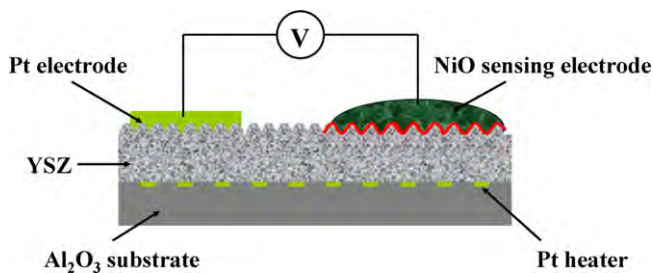**Fig. 1.** Three-phase boundary of sensor: (a) plane and (b) three-dimensional.

Fig. 2. Schematic view of the planar sensor.

Fig. 3. XRD pattern of NiO powders sintered at 1100 °C for 3 h in air.

In the present work, it was proposed to control the roughness of the surface of YSZ plate with the hydrofluoric acid corrosion. The correlation between the surface roughness of YSZ plate and the corrosion conditions (corrosion time and HF concentration) are investigated. The mixed potential type NO_2 sensors with high sensing performance was obtained by combining the rough YSZ plate with NiO sensing electrode, as shown in Fig. 1b. The sensing mechanism referred to the three-phase boundary was suggested.

2. Experimental

2.1. Fabrication of sensor device

The planar NO_x sensors were fabricated using YSZ plates (8 wt.% Y_2O_3-doped, 2×2 mm, 0.2 mm thickness, Tosoh Corp., Japan). YSZ plates were corroded by hydrofluoric acid (Beijing Chemical Works) with different concentrations (10%, 20% and 40%) for 3 h at room temperature [25]. A point-shaped and a narrow stripe-shaped Pt electrode were formed on the two ends of the as-corroded YSZ plate by applying the commercial Pt paste (Sino-platinum Metals CO., Ltd.). The nickel oxide powder was prepared by precipitation method and the obtained precursors were sintered at 1100 °C for 3 h [26]. The as-prepared NiO powder was mixed with pure water, and the resulted paste was coated on the point-shaped Pt electrode, followed by sintering at 1200 °C for 3 h. Then, a Pt heater formed on Al_2O_3 substrate was attached to the sensor device by chemical glue as shown in Fig. 2.

The crystal structure of the nickel oxide powder was confirmed by X-ray diffraction (Rigaku wide-angle X-ray diffraction D/max rA, using Cu Kα radiation at wavelength λ = 0.1541 nm) analysis. The surface topography of the YSZ plates corroded with HF was observed by means of field-emission scanning electron microscopy (FE-SEM; JEOL, JSM-7500, Japan) and Atomic Force Microscope (AFM; Being Nano-Instrument, Ltd., CSPM5500, China).

2.2. Evaluation of sensing properties

Gas sensing properties of the sensor were measured by a conventional static mounting method. The Pt heater offers the working temperature for the sensor. The sample gases containing different NO_2 concentration w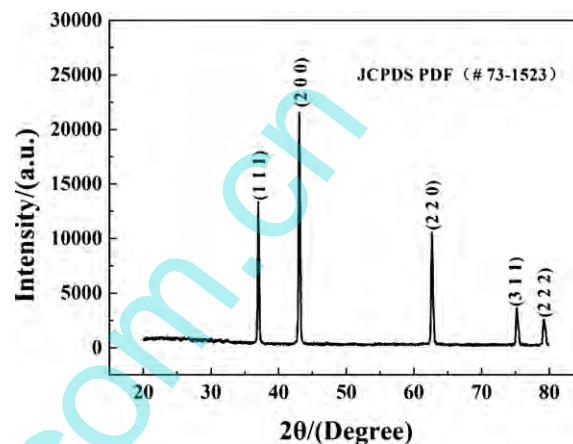ere obtained by diluting 10,000 ppm NO_2 with the base gas composed of O_2 (21 vol.%) and N_2 (79 vol.%). When the sensor was exposed to air or the sample gas, the potential difference was measured with a digital electrometer (Digital Multimeter; Rigol Technologies, Inc., DM3054, China) as the sensing signal, and the results were recorded with a computer connected to the electrometer [27–29].

The current–voltage (polarization) curves in the potential range of −50 to 110 mV were measured by means of potentiodynamic method at a constant scan-rate of 6 mV/min using a two-electrode configuration in the base gas (21 vol.% O_2 + N_2 balance) and the sample gas (100 and 200 ppm NO_2 + 21 vol.% O_2 + N_2 and balance) (Instrument corporation of Shanghai, China, CHI600C). The current axis of the anodic polarization curve was subtracted from that of the cathodic polarization curve at each potential so as to obtain the modified polarization curve in which the current axis is shown in absolute scale.

The complex impedance of the sensor in air or sample gas was measured by means of an impedance analyzer (Solartron, 1260 and Solartron, 1287) in the frequency range of 0.1 Hz–1 MHz. The amplitude of the ac potential signal was fixed at 250 mV in all measurements.

3. Results and discussion

3.1. Characterization of sensor materials

Fig. 3 exhibits the XRD pattern of NiO powders sintered at 1100 °C for 3 h in air. It can be seen that NiO retains its crystallographic phase (face-centered cubic) corresponding to JCPDS PDF (# 44-1159). Due to the sintering effect at elevated temperature, all the peaks assigned to NiO were very narrow. The mean grain size of NiO calculated by Debye–Scherrer equation was about 70 nm.

Fig. 4 shows the representative SEM images of the surface for the YSZ plates corroded with different concentrations of HF. It can be observed that the roughness of the surface for the corroded YSZ
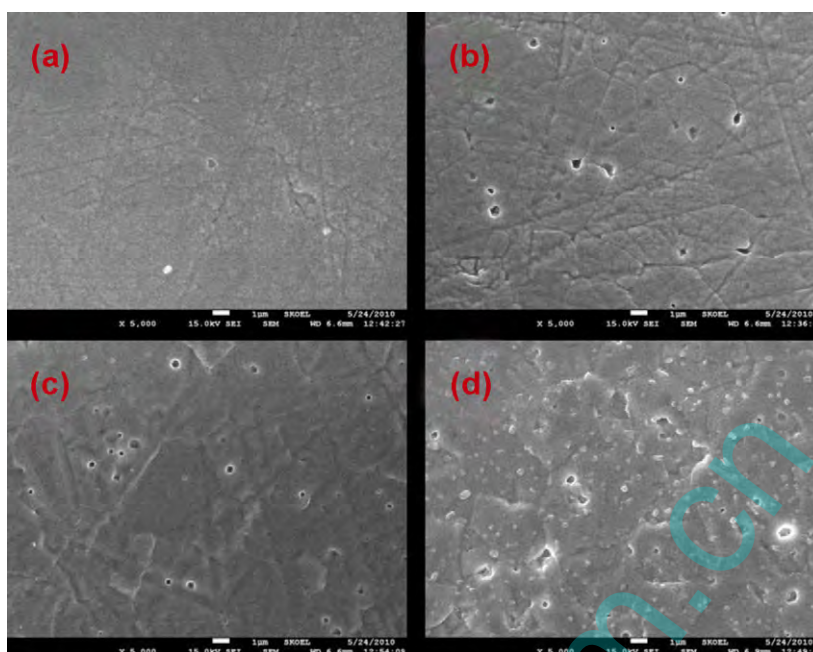
Fig. 4. (a–d) SEM images of the surface of YSZ treated with different concentration HF: (a) uncorroded, (b) 10% HF, (c) 20% HF and (d) 40% HF.

plate increases with the increase of HF concentration. The number of holes and ravines on the surface stands for the roughness, the much bumpier the surface is, the larger the contact area between YSZ plate and the sensing electrode. In order to prove that the roughness will increase with increase of the HF concentrations, AFM analysis was used to investigate the surface roughness of the plates as shown in Fig. 5. The surface root mean squares, which represent the roughness of the YSZ plate surface, are changed proportionally to the HF concentrations. The results prove the above conclusion.

3.2. Sensing performances of the NO_2 sensors

All sensors using the corroded YSZ plates and NiO electrodes were sintered at 1200 °C. The response and recovery transients to different concentrations of NO_2 for the sensors using the YSZ plates corroded with different HF concentrations are shown in Fig. 6. It can be seen that the change of potential difference (potential difference (NO_2)-potential difference (air)) to the same concentration NO_2 increases at 850 °C with the increase of the HF concentration. The value of the change of potential difference among the sensors using different corroded YSZ plates becomes larger with the increase of the NO_2 concentration. When the concentration of NO_2 is low (less than 20 ppm), the active sites on the three-phase boundary of each sensor are enough to supply the reaction field for full reaction with the sample gas, so the sensitivities of the sensors are almost independent of the HF concentrations. However, the number of the active sites on the three-phase boundary seemed to be affected by the roughness of the YSZ substrates, namely decided by the HF concentrations. Therefore, in high NO_2 concentration range (more than 50 ppm), the sensitivities to NO_2 strongly depend on the HF concentrations. It can also be seen that the response time for each sensor is about 3–5 s, but the recovery rate become slower with the increase of the surface roughness of the YSZ substrate. This can be attributed to the large contact area and good porosity which obstruct the desorption and diffusion process of the reaction products.

Fig. 7 shows the correlations between the potential difference and the logarithm of the NO_2 concentrations for the sensors.

The potential difference of the sensors is almost linear with the logarithm of the NO_2 concentration at 850 °C. The slope of the sensor using uncorroded YSZ plates is about 37 mV/decade, and the ones corroded by 10%, 20% and 40% HF are about 46, 50 and 76 mV/decade, respectively. It is obvious that the slope became larger with the increase of the HF concentration, and the sensor using the YSZ plate corroded with 40% HF shows the biggest slope. The slopes of the sensors using the corroded YSZ plates are rather larger, compared with the results reported by the other research groups. For example, the slope of planar NO_2 sensor using stabilized zirconia and NiO reported by Miura was about 22 mV/decade, which is smaller than our results [10]. This also indirectly indicates that the improvement of the effective area of three-phase boundary plays an important role in increasing the sensitivity (slope) of the sensor, although the oxide electrode is same. The inset in Fig. 7 exhibits the measured results in 1–9 ppm and 20–1000 ppm. The slopes in lower and higher ranges are very different. It can be found the chemical catalytic activity and thickness of oxide layer affected the sensing performance. It can be easily understood that part of the NO_2 will be consumed in the oxide layer before arriving at TPB and the change ratio of NO_2 conc. at TPB is larger in the lower NO_2 concentration compared with higher conc. This is why the slope in high NO_2 concentration is larger than low NO_2 conc. The present sensor device (treated with 40% HF) was further subjected to additional test for the response transients to 100 ppm NO_2 which was repeated six times at 850 °C. As shown in Fig. 8, the response transients as well as the potential difference response to 100 ppm NO_2 are almost reproducible in the successive runs.

The sensor using the YSZ plate corroded by 40% HF also exhibits well selectivity to NO_2 against the interference gases, such as NH_3, H_2, H_2S, Cl_2, C_4H_{10} and CH_4 at 850 °C (Fig. 9). The cross-sensitivities of the sensor to these interference gases are rather small or almost none and indicate excellent NO_2 selectivity. According to the mixed-potential sensing mechanism, the response directions to reducing and oxidation gases are positive and negative, respectively, if the reference electrode is opened to air only. We have noticed that the response directions of H_2 and CH_4 are positive, although these two gases are the typical reducing ones. Such results can be attributed to the planar structure of our sensor. For the pla-
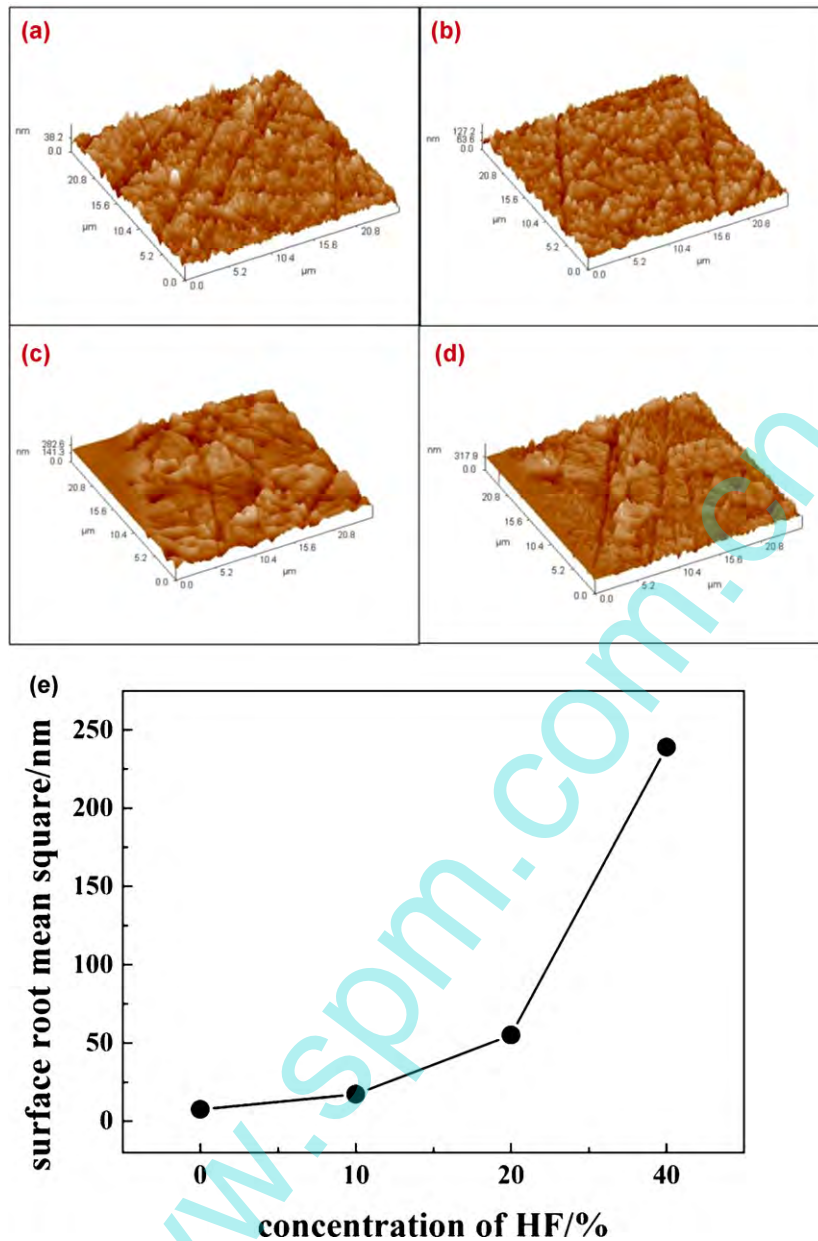
Fig. 5. (a–d) AFM images of the surface of YSZ treated with different concentration HF: (a) uncorroded, (b) 10% HF, (c) 20% HF, (d) 40% HF and (e) surface root mean square of different surface root mean square.
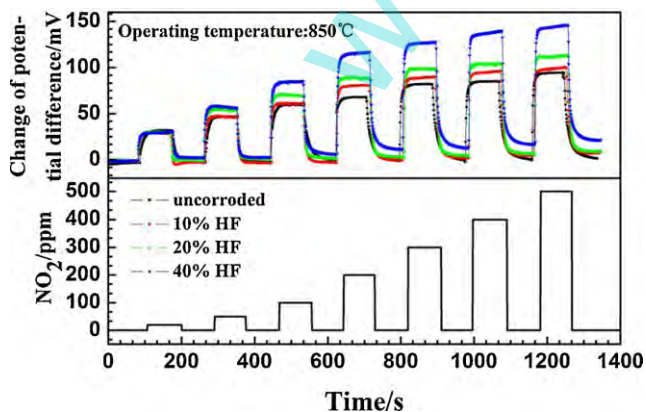

Fig. 6. The kinetic response of the sensor using YSZ treated with different concentration HF to 20–500 ppm NO$_2$.

nar type sensor, since both sensing electrode and reference one are exposed to the same atmosphere, the sensing signal is determined by the difference of the potentials at the sensing and reference electrodes. Generally, either sensing electrode potential or reference electrode potential is mixed potential under the detecting gases, the directions and values of the two mixed potentials are dependent on the sensing properties of these two electrode materials. If the reference electrode is more active than the sensing electrode to H$_2$ or CH$_4$, the response should be positive. In fact, Miura et al. have reported that the responses to CO and hydrocarbons are positive at 900 °C [10].

3.3. Sensing mechanism of the nitrogen dioxide sensor

As described above, the sensor gave a good linear relationship between potential difference and the logarithm of the concentration of NO$_2$ as switching on dilute NO$_2$ in Fig. 7. For the
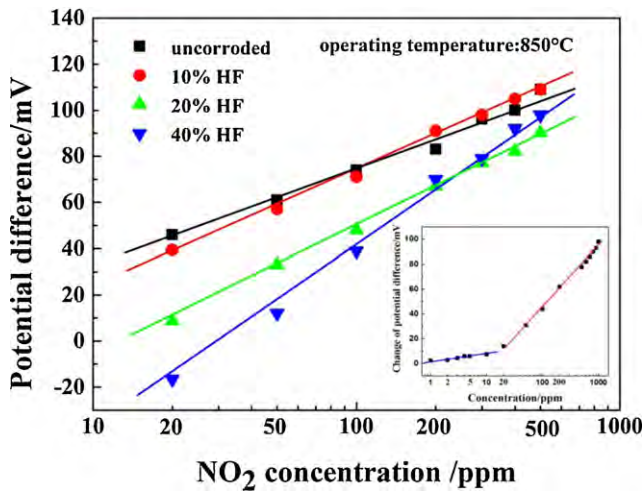
Fig. 7. Dependence of potential difference on the NO_2 concentration for the device using YSZ treated with different concentration HF.
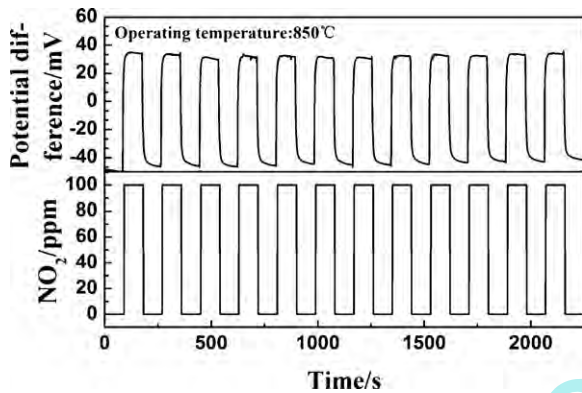

Fig. 8. Response transients of the sensor using the YSZ substrate that corroded by 40% hydrofluoric acid upon switching on- and off-NO_2 repeatedly at 850 °C.
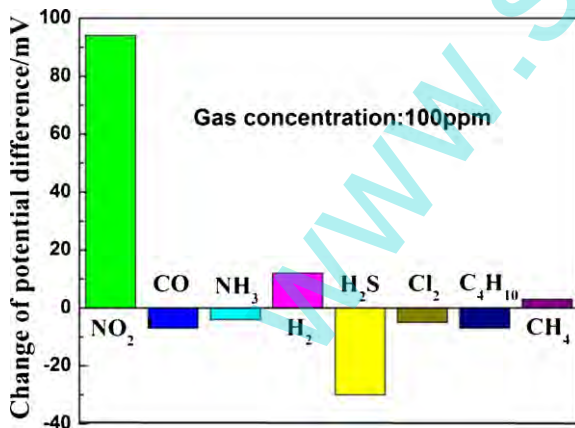

Fig. 9. Sensitivities of the sensor using the YSZ substrate that corroded by 40% hydrofluoric acid to various gases at 850 °C.

stabilized zicronia-based potentiometric sensors, two main sensing mechanisms have been proposed. At first, some groups suggested a mixed potential sensing mechanism involving the double electrochemical reactions at the sensing electrode [30–34]. This mechanism has been testified by the measurable polarization curves. On the other hand, Van Assche and Wachsman have proposed a "Differential Electrode Equilibria" sensing mechanism based on the formation of charge-building compounds for

a special sensing material (e.g. $LaCu_2O_4$) [35]. In this work, we attempted to explain for the sensing behavior of the potentiometric NO_x sensor using the corroded YSZ plate and NiO. This device can be described by the following electrochemical cells,

In air : O_2, NiO/YSZ/Pt, O_2

In sample gas : $O_2 + NO_2$, NiO/YSZ/Pt, $NO_2 + O_2$

Under the coexistence of NO_2 and O_2, a local cell is formed at the sensing electrode by the following electrochemical reactions:

Cathodic : $NO_2 + 2e^- \rightarrow NO + O_2^-$ (1)

Anodic : $2O^{2-} \rightarrow O_2 + 4e^-$ (2)

When the rates of the above two electrochemical reactions are equal, the sensing electrode potential is so-called mixed potential, the difference of the sensing and reference electrode potentials is measured as the sensing signal.

The magnitude of the mixed potential is strongly dependent on the kind, microstructure and layer thickness of the sensing materials. Three main factors play the key roles in determining the magnitude of the mixed-potential [30]. Firstly, high electrochemical catalytic activity of the sensing electrode material to NO_2 or NO is necessary for increasing the sensitivity. Secondly, inactivity to oxygen can reduce the rate of the reaction (2) and indirectly increase the magnitude of the mixed potential. In addition, high chemical catalytic activity of the sensing material to the reaction $NO_2 \rightarrow NO + 1/2O_2$ is negative for the mixed-potential, because the NO_2 will be consumed in the diffusion process of NO_2 through the sensing electrode layer.

All the above-mentioned factors are entangled with each other in a complicated manner, finally determined the sensitivity to NO_x. In this work, we paid special attentions for the microstructure of the triple-phase-boundary and tried to enhance the double of electrochemical reactions (1) and (2) by enlarging the contact area of YSZ and the sensing electrode. Larger contact area can supply more electrochemically active sites for the reactions (1) and (2), finally result in the increase of the sensitivity to NO_2 at elevated temperature. In our previous works, we obtained the correlation between the mixed potential and the concentrations of NO_x and oxygen according to the mixed-potential sensing model. In the case of detecting NO_2, when the NO_2 concentration is fixed, the mixed-potential is linear with the logarithm of the O_2 concentration in a minus slope. For the present sensor, in order to verify this conclusion, the effect of the coexisting oxygen concentration was investigated. Fig. 10(a) shows the response transient to 100 ppm NO_2 in atmospheres containing 2%, 5%, 10%, 20% O_2 at 850 °C. As expected, the response transients reduced with the increasing concentration of O_2, the same results are plotted in Fig. 10(b). It is observed that the potential difference is almost linear to the logarithm of the O_2 concentration and the slope is negative. Such a result examined the sensing mechanism involved in the mixed-potential.

In order to further testify the mixed-potential-model, the polarization curves of the sensors using the untreated YSZ plate and the treated one with 40% HF were measured in air and $NO_2 +$ air. The anodic polarization curve was obtained in air, and the cathodic polarization curve was obtained by subtracting in air from in $NO_2 +$ air. The modified polarization curves of the sensors using the untreated YSZ plate and treated one are shown in Fig. 11(a) and (b). The mixed-potential can be estimated from the intersection of the anodic and cathodic polarization curves. In Table 1, we compared the estimated values and the measurable potential difference for the two sensors. It is clear that the estimated values are very close to the potential difference values experimentally observed. These
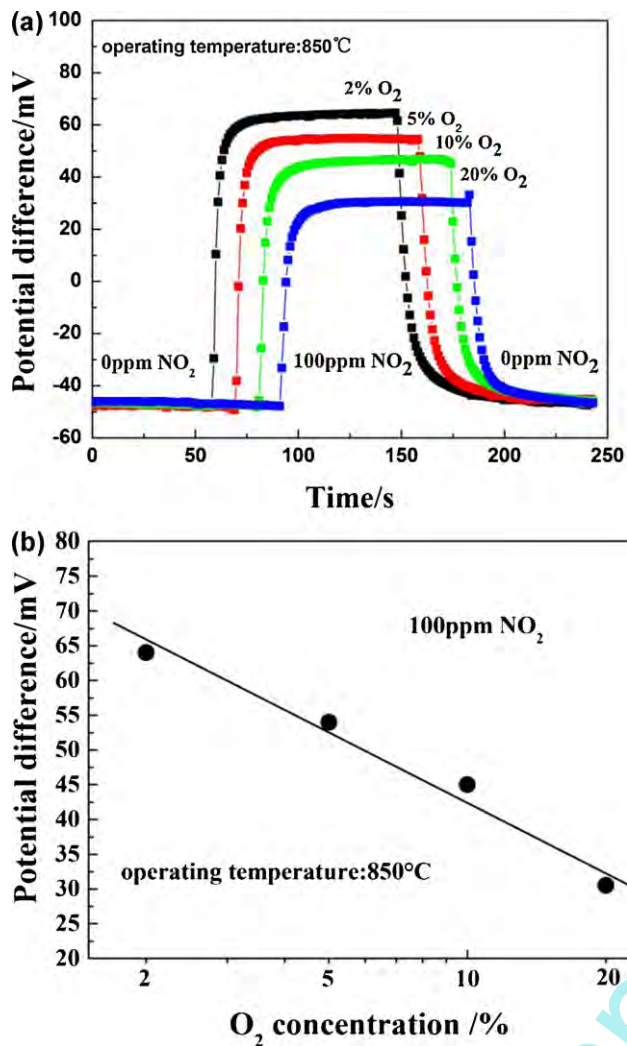
Fig. 10. (a) The kinetic response of the sensor using the YSZ substrate that corroded by 40% hydrofluoric acid to O_2 and (b) dependence of potential difference on the O_2 concentration.

Table 1
Comparison between mixed potentials estimated and potential difference values observed for the sensors using the untreated YSZ plate and the treated one with 40% HF at 850 °C.

Sensor	NO_2 conc. (ppm)	Mixed potential (estimated) (mV)	Potential difference value (observed) (mV)
Untreated	100	75	74
	200	85	83
Treated	100	41	39
	200	68	70

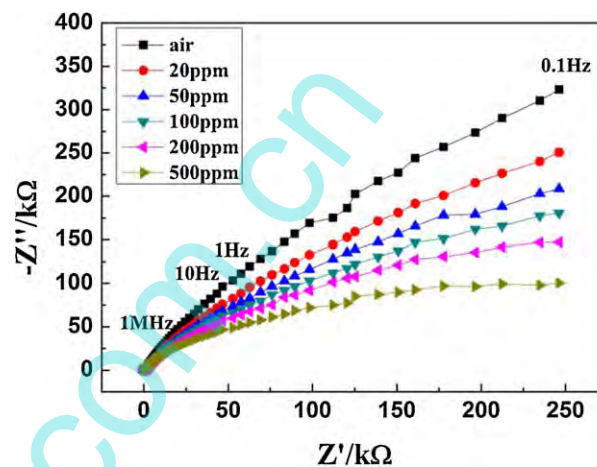**Fig. 12.** Complex impedance plots in the base air and the sample gas with each of various concentrations of NO_2 for the sensor.

results supply a new evidence for the mixed-potential potential model.

Fig. 12 shows the complex impedances of the sensor at 850 °C both in air and the sample gases containing various concentrations of NO_2. The complex impedance values (|Z|) at low frequency (around 0.1 Hz) decrease with an increase of NO_2 concentrations. In contrast, the |Z| values at high frequency (around 1 MHz) are almost invariant with different concentrations of NO_2. The varying frequencies of the voltage between the electrodes are so high that the rate of the electrochemical reactions cannot keep up with them, while at the low frequency, the time for the electrochemical reactions is long enough. So it can be proved that the most of the electrochemical reactions occurred in the interface. In the present case, the appearance of NO_2 sensitivity seems to be also attributable to the change in the resistance of electrochemical reaction at the interface between YSZ and NiO electrode [36,37]. Thus, it can be concluded that most of the electrochemical reactions occur at the three-phase boundary.
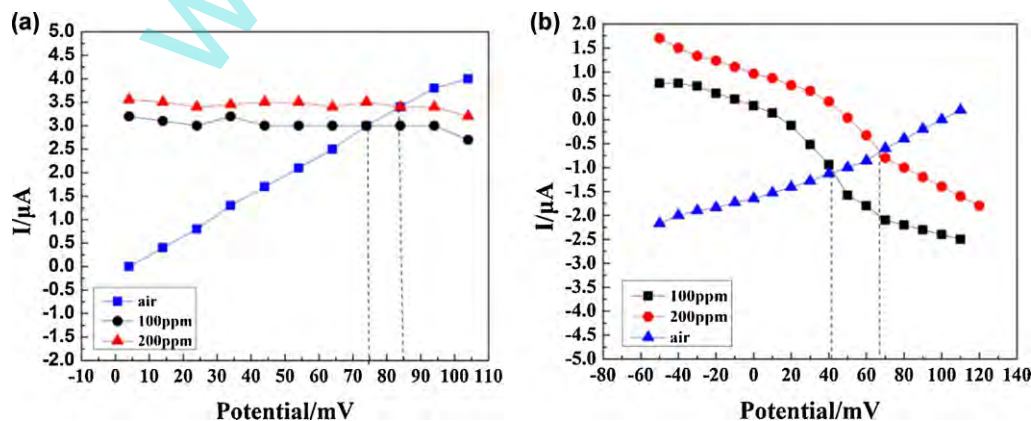

Fig. 11. Polarization curves recorded in air, in 100 and 200 ppm NO_2 at 850 °C for the sensor: (a) using the YSZ substrate untreated and (b) using the YSZ substrate that corroded by 40% hydrofluoric acid.

4. Conclusions

The conjecture that the sensing characteristics of mixed-potential-type NO_2 sensor based on an yttria-stabilized zirconia (YSZ) plate can be improved by increasing superficial area of three-phase boundary is tested and verified in this work. Surface topography of YSZ substrate was improved by the corrosion with different concentrations of hydrofluoric acid (10%, 20%, and 40%) for 3 h. Through investigating the sensing properties of the NO_2 sensors at 850 °C, it is found that the sensitivity to 20–500 ppm NO_2 is as high as 76 mV/decade for the sensor using the YSZ substrate corroded with 40% HF. Moreover, the sensor exhibits well selectivity and rapid response–recovery characteristics to NO_2. The dependence of the O_2 concentration, polarization curves and complex impedances of the device indicate that the NO_2 sensing behavior can be well explained by the mixed potential model.

Acknowledgments

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