A GdAlO$_3$ Perovskite Oxide Electrolyte-Based NO$_x$ Solid-State Sensor

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NO$_x$ is a notorious emission from motor vehicles and chemical factories as the precursor of acid rain and photochemical smog. Although zirconia-based NO$_x$ sensors have been developed and showed high sensitivity and selectivity at a high temperature of above 800 °C, they fail to show good performance, and even don’t work at the typical work temperature window of the automotive engine (<500 °C). It still is a formidable challenge for development of mild-temperature NO$_x$ detector or sensor. Herein, a novel amperometric solid-state NO$_x$ sensor was developed using perovskite-type oxide Gd$_{1−x}$Ca$_x$AlO$_3$$_δ$ (GCA) as the electrolyte and NiO as the sensing electrode. NO$_x$ sensing properties of the device were investigated at the temperature region of 400–500 °C. The response current value at $-300$ mV was almost linearly proportional to the NO$_x$ concentration between 300 and 500 ppm at 500 °C. At such a temperature, the optimal sensor gave the highest NO$_2$ sensitivity of 20.15 nA/ppm, and the maximum response current value reached 5.57 μA. Furthermore, a 90% response and 90% recover time to 500 ppm NO$_2$ were about 119 and 92 s, respectively. The excellent selectivity and stability towards NO$_x$ sensing showed the potential application of the sensor in motor vehicles.

The nitrogen monoxide (NO) and nitrogen dioxide (NO$_2$), referred as NO$_x$, are one kind of the most hazardous air pollutants causing acid rain and photochemical smog. A major source of NO$_x$ emission is from automobile exhaust, and as a result, the NO$_x$ emission sharply inclined due to the rapid increase of the amount of automobiles worldwide. Therefore, detection and monitoring of NO$_x$ gas is an important operation in environmental protection. Computerized control of internal combustion engines has improved the work efficiency and decreased the emission of NO$_x$ gas, where the sensor tracing nitrogen oxide (NO$_2$) is the key to the closed loop feedback control of the emissions.

Development of NO$_x$ sensors based on solid electrolytes has attracted great attention recently. The solid electrolytes mainly include two categories: fluorite (AO$_2$)-type and perovskite (ABO$_3$)-type electrolyte. The traditional solid electrolytes for sensing NO$_3$ are zirconia-based ceramics with the fluorite (AO$_2$)-type structure. Until recently, Yttria stabilized Zirconia (YSZ) based sensors aroused great attention due to their great sensitivity, excellent selectivity, response signal testability, simple structure, the superiority on a wide gas test range, and particularly, the operating ability under high-temperature and hazardous conditions. Miura et al. fabricated an amperometric-type NO sensor using YSZ substrate with oxide electrode (CdCr$_2$O$_4$), which showed quick and selective response to NO. Park et al. reported a mixed-potential-type NO$_x$ sensor using the YSZ electrolyte with a CuO electrode showing good transient responses and large response values. However, the YSZ-based sensors show high oxygen-ion conductivity only above 800 °C. The high operating temperature can lead to a series of problems such as electrode aging, adverse reactions and interfacial diffusion between electrode and electrolyte, weak long term stability and high cost of interconnects and other issues. This greatly limits the application of such sensors in NO$_x$ detection. Therefore, it is urgent to search an alternative solid electrolyte material that can work for sensing NO$_x$ at a mild temperature.

Recently, many mild-temperature NO$_x$ sensors have been studied. For example, Wang et al. investigated the Pt/La$_{0.75}$Sr$_{0.25}$NbO$_{2.75}$ (LSNO)/NiO sensor and showed that the sensor had a very high sensitivity to NO$_2$ at the operating temperature of 450–600 °C. Dai et al. also fabricated an amperometric-type NO$_x$ sensor using Ca$_{0.9}$Gd$_{0.1}$O$_{3-δ}$ (CGO) substrated with La$_{0.75}$Sr$_{0.25}$Cr$_{0.5}$Mn$_{0.5}$O$_{3-δ}$ (LSCM) sensing electrode, which gave the high NO$_2$ sensitivity of 134 nA/ppm at 500 °C. In addition, Ueda et al. reported that the electrochemical gas sensor

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Pt/YSZ/La0.6Sr0.4Co0.98Mn0.02O3, which demonstrated the fast response to NO2 at 500–600 °C, but the response current value had only 3 μA to 400 ppm NO2 at 550 °C.

At present, perovskite (ABO3)-type oxides have been widely studied as potential candidates for gas sensing. Structurally, the AO2 type oxides only offer A site for aliovalent ion doping. However, not only the perovskite oxides provide A site but also B site for doping, thus vacancies in the oxygen sublattice are more easily formed and the higher conductivity can be achieved. For example, the oxide ion conductivity exhibiting in the doubly-doped La0.8Sr0.2Ga0.83Mg0.17O2.815 (LSGM) perovskite oxide is three times higher than 8YSZ at 800 °C. Sinha et al. showed that calcium-doped GdAlO3 is promising material for oxygen-ion-conducting solid electrolyte application. Among the doped systems, Gd0.85Ca0.15AlO3−δ showed a conductivity of 0.057 S/cm at 1000 °C, which was only slightly less than that of yttria-stabilized zirconia at the same temperature. Moreover, the gadolinium aluminate material was widely applied in different luminescent display systems, neutron absorption, and control rod. It was also reported that the gadolinium aluminate material could be applied to the solid oxide fuel cell. However, to the best of our knowledge, no reports were found on NOx sensors that are prepared using calcium-doped GdAlO3 system as solid electrolyte.

In this paper, an amperometric NOx sensor was fabricated using perovskite-type oxide Gd1−xCaxAlO3−δ (GCA) as an electrolyte, NiO as sensing electrode (NiO-SE), and a noble metal Pt as reference electrode (Pt-RE), as illustrated in Fig. 1. The GCA powder was synthesized by citrate gel route. The advantage of citrate gel route over the conventional solid-state synthesis method, particularly for singly and doubly doped GdAlO3 compositions, is that it tunes at a molecular level and produces solid powders that could be sintered to have good densities at significantly lower temperatures. NOx sensing performance of the device was measured on the Electrochemical Workstation to study its sensitivity, selectivity and stability at the temperature range of 400–500 °C.

Figure 1. (a) Schematic representation of the fabricated sensor, (b) top view of the sensor, (c) bottom view of the sensor.
$n\lambda = 2d_{hkl}\sin\theta$, where $d_{hkl} = \frac{1}{\sqrt{a^2 + b^2 + c^2}}$.

(1)

Here, $n$ is the diffraction order, $\lambda$ is the x-ray wavelength, $d_{hkl}$ is the interplanar distance, $(h k l)$ are the Miller indices for the corresponding $d$-spacings and $a$, $b$, $c$ are the lattice parameters.

Additionally, it can be observed that with increasing $x$, the three peaks of {020, 112, 200} are gradually merged into one peak and decreased in intensity. The gradual broadening and weakening are mainly originated from the lattice disordering. For $x = 0.2$, the {112} Bragg diffraction peak is nearly coincided with $x = 0.0$. It was attributed to the phase change of GdAlO$_3$ doped with Ca$^{2+}$ ion, leading to the formation of a new matter, GdCaAl$_3$O$_7$, due to the dissociation of doped Ca$^{2+}$ ions from the GdAlO$_3$ lattice structure. The most different point is that the $2\theta$ position of the {112} peak recovers for $x = 0.2$, but the broadening and weakening of these diffraction peaks are reserved, suggesting that the local structural disordering is maintained by the formation of oxygen vacancies.

Figure 3 shows the IR spectra of the samples prepared by calcinations of gel precursors for 4 h at 1500 °C: (a) $x = 0$, (b) $x = 0.05$, (c) $x = 0.1$, (d) $x = 0.15$, and (e) $x = 0.2$. It was observed that the spectra measured at different Ca-doped concentrations are basically the same except for a systematic data shift. The IR spectra showed strong bands at 660 and 465 cm$^{-1}$ which are characteristic M-O (possibly Gd-O and Al-O stretching frequencies) vibrations for the perovskite structure compounds$^{40}$. Additionally, it was noted that the Ca-doped samples showed three new peaks at 815, 870, and 924 cm$^{-1}$ and the peaks at 660 cm$^{-1}$ moved to a higher wave number with increasing $x$. It has been reported that the size-induced lattice variations and the concentration of oxygen vacancies might lead to a red shift of IR absorption$^{40,41}$. For the Gd$_{1-x}$Ca$_x$AlO$_{3-\delta}$ systems, since the diameter size of Ca$^{2+}$ ion is bigger than that of Gd$^{3+}$ ion, it results in the lattice expansion and formation of oxygen vacancies. The Ca-doped GdAlO$_3$ point defect reaction could be written as Eq. 2$^{45}$:

$$2CaO + 2V_{Gd}^\text{tr} + 3V_{O}^* \rightarrow 2Ca_{Gd}^\text{tr} + 2O_{O}^\text{X} + V_{O}^*$$

(2)
Here, with increasing $x$, the concentration of mobile oxygen vacancies increased. Moreover, these new IR peaks are originated from the formation of some new chemical bonds by introduction of calcium. The above results suggested that Ca$^{2+}$ ions have entered into the perovskite lattice structure.

Figure 4 shows the SEM images of the surfaces of Gd$_{1-x}$Ca$_x$AlO$_{3-\delta}$ substrates calcined at 1500 °C for 4 h ($A$) $x = 0.05$, the inset shows the $x = 0$, ($B$) $x = 0.1$, ($C$) $x = 0.15$, and ($D$) $x = 0.2$.

Sensing performance of the devices. This sensor based on the solid electrolyte substrates can be shown as the following electrochemical cells in the presence of O$_2$ and NO$_2$: ($-)\ O_2 + \text{NO}_2, \text{NiO/GCA/Pt}, \text{NO}_2 + \text{O}_2 (+)$. When the sensor was exposed to the sample gas, the response current value changed at the fixed potential of $-300$ mV. The following electrochemical reactions would occur at the triple-phase boundary (TPB, among gas/sensing electrode/electrolyte) and counter electrode in a series of physisorption and charge exchange reactions, as described by Eq. 3 and Eq. 4.

\[
\text{Cathode: } \text{NO}_2 + 2\text{e}^{-} \rightarrow \text{NO} + \text{O}^{2-} \quad (3)
\]

\[
\text{Anode: } 2\text{O}^{2-} \rightarrow \text{O}_2 + 4\text{e}^{-} \quad (4)
\]

Amperometric response and recovery transients to 500 ppm NO$_2$ with a polarized potential of $-300$ mV at 400, 450, and 500 °C for the sensor based on Gd$_{0.85}$Ca$_{0.15}$AlO$_{3-\delta}$ substrate were shown in Fig. S2. As well known, if you choose the cathode to be positive in the software setup, and a negative voltage of $-300$ mV is applied in the work, you will obtain a positive current. As seen from Fig. S2, the baseline current increased with increasing temperature due to some reactions of low level impurities at electrode and slight electric conductive contribution, which was in agreement with the result reported by Wang et al.$^{43}$

Figure 5A shows the response transients of the sensor based on Gd$_{1-x}$Ca$_x$AlO$_{3-\delta}$ substrates at 500 °C under various NO$_2$ concentrations in the range between 300 to 500 ppm in the presence of 5 vol. % O$_2$, when the potential of $-300$ mV was applied. In order to better distinguish the response curve, the base current levels have been shifted. At each NO$_2$ concentration, a large increase in response current value was observed in the case of the sensor based on Gd$_{1-x}$Ca$_x$AlO$_{3-\delta}$ substrate. For instance, the response current value of the sensor based on Gd$_{0.85}$Ca$_{0.15}$AlO$_{3-\delta}$ substrate was $0.93\mu$A for 300 ppm NO$_2$ at 500 °C. When the NO$_2$ concentration went up to 400 ppm, the response current value inclined to $1.78\mu$A. For the NO$_2$ sensor in this study, the NiO sensing electrode showed a strong adsorption and catalytic activity for NO$_2$. An increase of the NO$_2$ concentration brought enhancement of NO$_2$ adsorption on the sensing electrode, which would produce more oxygen ions (O$^{2-}$) through the cathodic reaction of Eq. 3 and thus the response current of the sensors was improved.

In this work, the response current value was defined as the difference of current value between the sample gas and base gas ($\Delta I = I_{\text{gas}} - I_{\text{base}}$, where $I_{\text{gas}}$ and $I_{\text{base}}$ referred to the current values in the targeted concentration C ppm and 0 ppm NO$_2$). Figure 5B shows the relationship between the response current of the sensor based on
Gd$_{1-x}$Ca$_x$AlO$_{3-δ}$ substrate and the NO$_2$ concentration at a bias potential of $-300$ mV. It can be seen that the response current value was almost linear to the NO$_2$ concentration from 300 to 500 ppm for the sensor based on Gd$_{1-x}$Ca$_x$AlO$_{3-δ}$ substrate at 500 °C. The sensitivity of the sensor is defined as the ratio of response current to NO$_2$ concentration. For $x = 0.05–0.15$, the sensitivity of the sensor was enhanced with increasing the Ca doping. For example, the sensitivities of the sensors based on Gd$_{1-x}$Ca$_x$AlO$_{3-δ}$ substrate with $x = 0.05$, 0.1 and 0.15 were 5.71, 11.58 and 20.15 nA/ppm at 500 °C, respectively. Nevertheless, the sensitivity of the sensor based on the Gd$_{0.8}$Ca$_{0.2}$AlO$_{3-δ}$ substrate declined to 19.22 nA/ppm because of over-doping. Compared to the response transient of the reference sensor based on YSZ-8 substrate to 500 ppm NO$_2$ in the presence of 5 vol% O$_2$ at 500 °C (see Supplementary Fig. S3), the sensor based on Gd$_{1-x}$Ca$_x$AlO$_{3-δ}$ substrates showed the potential application in motor vehicles.

Figure 6A shows the response transients of the sensor based on Gd$_{1-x}$Ca$_x$AlO$_{3-δ}$ substrates to 500 ppm NO$_2$ in the presence of 5 vol% O$_2$ at 500 °C (applied potential $-300$ mV, flow rate 200 cm$^3$/min): (a) $x = 0$, (b) $x = 0.05$, (c) $x = 0.1$, (d) $x = 0.15$, (e) $x = 0.2$. (B) and (C) showed the enlarged portions of (A) response transients in the range between 600 to 1200 s; (D) the effect of calcium doping on the response current value of gadolinium aluminate system in 500 ppm NO$_2$ at 400–500 °C.
Ca-doped GdAlO$_3$ sensors were one order magnitude higher than that of the undoped GdAlO$_3$. The increase in current values of the undoped sample was $0.43 \times 10^{-6}$, while that of the doped sample was $0.15 \times 10^{-6}$ at 400 °C. With increase of Ca doping, $\Delta I$ reached 0.31, 0.61 and 0.93 μA for $x = 0.05$, 0.1, and 0.15 at 400 °C, respectively. However, $\Delta I$ of $x = 0.2$ dropped to 0.7 μA, suggesting that $\Delta I$ greatly increased by doping Ca. As seen from Fig. 6D, $\Delta I$ was enhanced with increasing the operating temperature. The sensor based on Gd$_{0.85}$Ca$_{0.15}$AlO$_3$ substrate exhibited the highest $\Delta I$ value of 5.57 μA at 500 °C. The response currents of the Ca-doped GdAlO$_3$ sensors were one order magnitude higher than that of the undoped GdAlO$_3$. The increase in current value may be attributed to the increased conductivity of the Ca-doped GdAlO$_3$ substrates. For the perovskite-type oxides, tolerance factor $t$, can be used for describing the relationship between symmetry and ionic radii (Eq. 5):

$$ t = \frac{r_A + r_O}{\sqrt{2} (r_B + r_O)} $$

(Eq. 5)

Here, $r_A$ is the ionic radii of Gd$^{3+}$, $r_B$ is the ionic radii of Al$^{3+}$, and $r_O$ is the ionic radii of O$^{2-}$. Theoretically, when $t$ is equal to 1, the orthorhombic structure of perovskite-type GdAlO$_3$ will be altered to a cubic structure with a higher symmetry. The Ca doping made $t$ approach to 1, as result of the larger ionic radius of Ca$^{2+}$ (0.134 nm) than that of Gd$^{3+}$ (0.127 nm) of GdAlO$_3$, for coordination number 12$^6$, consequently enhancing the conductivity of GdAlO$_3$. Furthermore, by the Ca doping, the cell volume of the perovskite will increase and the concentration of mobile oxygen vacancies that assist the mobility of oxygen ion will increase. In brief, for $x = 0.05–0.15$, the Ca doping GdAlO$_3$ solid electrolyte is favorable for conductive properties of the sensor, whereas for $x = 0.2$, the conductivity begins to decrease due to the formation of impurity phase.

The selectivity is defined as the response discrepancy of an indicated gas from a mixed gas. Here, the selectivity factor is defined as $S = I_A/I_B$, where $I_A$ and $I_B$ are the responses of a sensor to a target gas A and an interference gas B, respectively$^{45}$. To evaluate the selectivity, the responses of the sensor based on Gd$_{0.85}$Ca$_{0.15}$AlO$_{3-\delta}$ substrate to CO, CH$_4$, C$_2$H$_6$, C$_3$H$_8$, and C$_2$H$_4$ were examined. Figure 7 shows the responses of different gases with a concentration of 500 ppm. It was observed that the sensor exhibited a high sensitivity and selectivity towards NO$_2$ gas compared to the other gases. The $\Delta I$ value of interference gases was fairly small in comparison with that of the sensor responding to NO$_2$ gas. For example, the $\Delta I$ values of NO$_2$, CO, CH$_4$, C$_2$H$_6$, C$_3$H$_8$, and C$_2$H$_4$ were 5.57, 7.7 × 10$^{-2}$, 4.20 × 10$^{-2}$, 9.80 × 10$^{-2}$, 2.13 × 10$^{-1}$, and 8.97 × 10$^{-2}$ μA at 500 °C, respectively. And the selectivity factors to CO, CH$_3$, C$_2$H$_6$, C$_3$H$_8$, and C$_2$H$_4$ were 72.34, 132.62, 56.84, 26.15, and 62.10, respectively. The influence of O$_2$ flow on CO, CH$_4$, C$_3$H$_8$, C$_2$H$_4$ and C$_3$H$_6$ were 72.34, 132.62, 56.84, 26.15 and 62.10, respectively. The response and recovery times are important parameters used to characterize a sensor. The response time is defined as the time that the resistance of the sensor reaches to 90% of the saturation value when the sensor was exposed to the base gas. The current values of the undoped sample was 4.20, 8.34, 7.23, 8.93, and 5.50 μA at 400, 450, and 500 °C, respectively. The response and recovery times initially cut down along with the Ca doping. The response time for Gd$_{0.85}$Ca$_{0.15}$AlO$_{3-\delta}$ substrate was measured for 3 h upon exposure to 500 ppm NO$_2$ gas with 5 vol. % O$_2$ at 450 °C (Fig. 8). The horizontal shows the centerline of the response current ripple. The as-prepared sensor shows a response current ($\Delta I$) of 5.57 μA. Furthermore, after the sensor was stored for half a month, a month, and two months, the response signal decreased slightly by 2.5%, 5.0% and 7.3%, respectively. The response current decreased by about 0.43 μA after the sensor was stored in ambient atmosphere for two months, compared to the as-prepared sensor. These results suggested that the sensor had a good stability.
Conclusions
In summary, an amperometric sensor based on Gd$_{1-x}$Ca$_x$AlO$_3$-$\delta$ substrates was developed. It showed excellent sensitivity to NO$_x$ gas at mild temperatures. The response current values of the sensor enhanced with increase of operating temperature. Furthermore, the sensitivity and response current values initially increased and then decreased with increasing the Ca doping. The Gd$_{0.85}$Ca$_{0.15}$AlO$_3$-$\delta$ sensor gave the highest NO$_2$ sensitivity of 20.15 nA/ppm and the highest response current value of 5.57 $\mu$A at 500 °C. Moreover, the sensor also exhibited a great selectivity and excellent stability.

Methods
Synthesis and analysis of GCA electrolytes. The Ca-doped GdAlO$_3$ powder was prepared through a citrate gel route$^{26,39}$, Gd(NO$_3$)$_3$·6H$_2$O (99.99% purity), Al(NO$_3$)$_3$·9H$_2$O (AR Grade), and Ca(NO$_3$)$_2$·4H$_2$O (AR Grade) were used as starting materials for preparation of Gd$_{1-x}$Ca$_x$AlO$_3$-$\delta$ (GCA) samples, where $x = 0, 0.05, 0.1, 0.15$, and $0.2$, respectively. The starting materials were taken with composition (Gd$_{1-x}$Ca$_x$)$_2$:Al = 1:1 molar ratio. For all the compositions, the molar ratio of total metal ion to citrate ion was kept 1. The gadolinium nitrate, aluminium nitrate and calcium nitrate were first dissolved in 250 mL distilled water at room temperature. Then citric acid as complex agent was added to the reaction solutions. Further, the mixed solution was slowly evaporated at 80 °C under stirring to form white transparent gel. The gel was further dried at 120 °C in an oven for 10 h to form precursor powder. After that, the powder was calcined at 1000 °C for 4 h.

The XRD data were first recorded on a Panalytical X’Pert Pro diffractometer at 40 kV and 40 mA using Co K$_\alpha_1$ ($\lambda = 0.178 901$ nm), then revised by Cu K$_\alpha_1$ ($\lambda = 0.154 056$ nm). The samples were scanned over a 2$\theta$ range from 10° to 100° with a step size of 0.0167° at a scanning rate of 10°·min$^{-1}$. The infrared spectra in the range of 1200–400 cm$^{-1}$ were recorded on a Thermo Fisher Scientific Nicolet 6700 FTIR device. The samples were prepared as KBr pellets.

Sensor fabrication and characterization. A NO$_2$ sensor was fabricated using NiO as sensing electrode (NiO-SE), which was synthesized by using the sol-gel method, perovskite-type oxide Gd$_{1-x}$Ca$_x$AlO$_3$-$\delta$ as electrolyte, and a noble metal Pt as reference electrode (Pt-RE). Pellets with 8 mm in diameter and 3 mm thickness were produced by applying 150 Mpa pressure to the calcined powders, and then sintered at 1500 °C for 4 h in the air. The NiO-SE was made from NiO paste, and a Pt wire (0.2 mm diameter) was attached to the NiO layer as a current collector. In addition, the Pt-RE was formed by using platinum paste, which was painted onto polished surface of GCA pellet which was on the other side, and then a Pt wire (0.2 mm diameter) was attached to the Pt surfaces. Subsequently, the sample was fired at 1000 °C for 1 h in air to get the NiO/GCA/Pt sensor.

Scanning electron microscopy (SEM, HitachiS4800 instrument) was applied for observing the morphology of the samples.

Evaluation of sensing properties. The fabricated sensor was assembled in a quartz tube and the sensing properties were evaluated in a conventional gas-flow apparatus equipped with a furnace operating at temperatures in range of 400–500 °C (see Supplementary Fig. S5). The gas environment consisted of a changing concentration of NO$_2$ (0–500 ppm) with base gases (O$_2$+N$_2$ balance) at a total flow rate of 200 cm$^3$/min.

The amperometric responses of the sensors were carried out using a potentiostatic method at $-300$ mV. The foremost electrochemical measurements were carried out by the Electrochemical Workstation (Instrument corporation of Shanghai, China, CHI600E).

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Author Contributions
Yihong Xiao and Fulan Zhong conceptualized the idea and device design. Dongmei Wang and Fulan Zhong performed the experiments and the data analysis. Dongmei Wang wrote the main manuscript text. Guohui Cai and Yong Zheng involved in correction of the manuscript. All the authors discussed the results and reviewed the manuscript.

Additional Information
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