NO$_2$ adsorption behaviour on LaFeO$_3$ electrodes of YSZ-based non-nernstian electrochemical sensors

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Abstract X-ray photoelectron spectroscopy (XPS) was used to examine the NO$_2$ adsorption behaviour on the LaFeO$_3$ and Pt electrodes of planar yttria stabilized zirconia non-Nernstian gas sensors. The electrochemical sensors were exposed to the same gas atmosphere containing 1000 ppm NO$_2$ at 650°C. XPS of the as-prepared sensors and sensors after exposure to NO$_2$ revealed bonded nitrogen peaks on the surface of the semiconducting oxide but no nitrogen peaks on the Pt electrode. Therefore, NO$_2$ adsorption on a LaFeO$_3$ electrode plays an important role in the NO$_2$ detection mechanism.

Keywords LaFeO$_3$ · YSZ · Non-Nernstian Electrochemical Sensors · XPS

1 Introduction

The sensing mechanism of these non-Nernstian sensors can be explained using the "mixed potential" theory [1–6]. The mixed potential mechanism has been claimed both for NO$_x$

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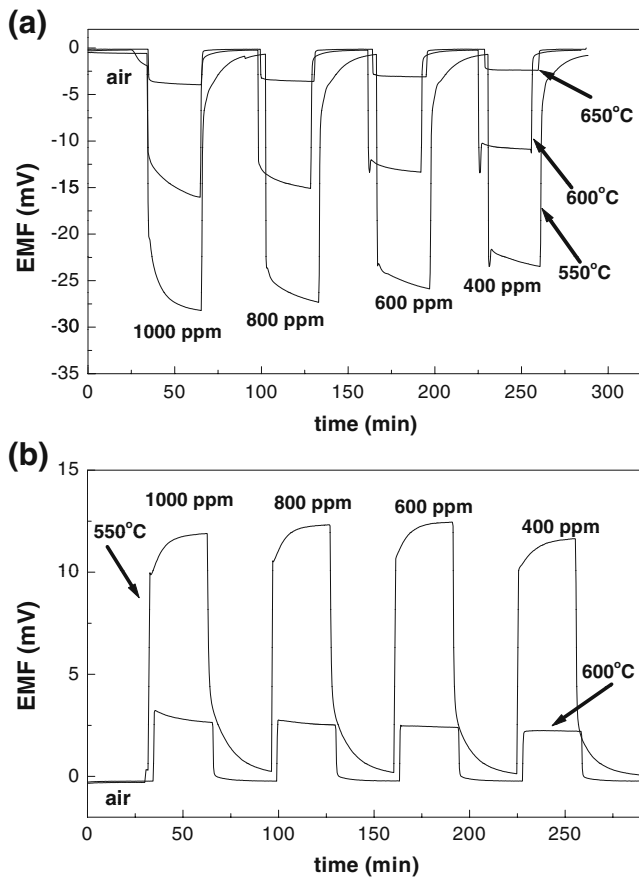Tsukuba, Ibaraki 305-0047, Japan

[1–3] and CO/HCs [4–6] gas sensors based on electrochemical cells with different metal oxide electrodes.

However, other phenomena need to be considered when semiconducting oxides are used as sensing electrodes, such as the surface morphology, electrocatalytic activity, adsorption-desorption behaviour of the electrodes, etc. Therefore, another gas sensing mechanism has been proposed; "differential electrode equilibria" [7]. This is a more general concept for explaining the gas sensitivity that is due not only to the electrochemical reactions, but also to different electrocatalytic activity and/or adsorption-desorption behaviour of the two electrodes.

Some of the authors of this paper previously examined the sensing properties of electrochemical sensors based on coupling YSZ with p-type (LaFeO$_3$), n-type semiconducting oxides (WO$_3$, In$_2$O$_3$) and mixed ionic-electronic conductors (La$_x$Sr$_{1-x}$FeO$_3$) [8–12]. The sensors were fabricated using either pellets or thick layers of YSZ to obtain devices in bulk and planar form. All sensors were exposed to the same atmosphere without reference air. The sensing mechanism of the sensors was examined. The results showed that in the case of a planar geometry (sensors with two parallel finger electrodes on the same side of tape-cast YSZ), the mixed potential theory could explain the EMF results: sensors with p-type semiconducting oxide electrodes showed opposite EMF values to those measured using sensors with n-type electrodes when exposed to the same gas [11]. When close and parallel finger electrodes were exposed to the same gas atmosphere, electrochemical reactions occurred on both electrodes at the same rate, and the adsorption mechanism characteristics of semiconducting oxides dominated the gas sensing behaviour [11].

This study examined the NO$_2$ adsorption behaviour on a LaFeO$_3$ electrode to determine the sensing mechanism of these types of sensors. XPS was performed on the surfaces

Fig. 1 (**a**) EMF response of the LaFeO₃ based sensors to different concentrations of NO₂ at different operating temperatures. (**b**) EMF response of the LaFeO₃ based sensors to different concentrations of CO at different operating temperatures

2 Experimental procedures

YSZ (8 wt.% of Y_2O_3) tape-cast layers, 8 mm×10 mm× 150 μm in size, were used as the solid electrolyte for the sensor fabrication [12]. Two parallel Pt finger electrodes were deposited on one side of the solid electrolyte at a distance of approximately 5 mm and fired at 750°C for 10 min. Nano-sized LaFeO₃ perovskite oxides, prepared in the laboratory [13], were mixed with a screen-printing oil and the slurry obtained was painted on an area of one metallic electrode and fired at 750°C for 3 h. The EMF measurements were performed at fixed temperatures ranging from 550 to 650°C at different NO₂ concentrations in air [14]. The surface chemical states and composition of the samples were characterized by XPS (PHI, 5600ci, using Al K_α excitation source) measurements. All the binding energies (BE) were referenced to the C 1 s photoelectron line at 284.5 eV. Surface

analysis was carried out both on the as-prepared sensors and the sensors exposed to 1000 ppm of NO₂ in air.

3 Results and discussions

The electrical measurements for the LaFeO₃-based sensors showed that upon exposure to NO₂ and CO, the EMF response was in opposite directions [11], i.e. negative EMF values upon NO₂ exposure, positive values upon CO exposure, as shown in Fig. 1. In turn, upon exposure to the same gas, the EMF values were opposite to the values measured using the WO₃-based sensors. These EMF results on planar sensors cannot be explained by the mixed potential theory. Several reports [15–17] have suggested that the sensing mechanism of solid-state electrochemical sensors with semiconducting electrodes can be explained by mixed potential theory. The following electrochemical
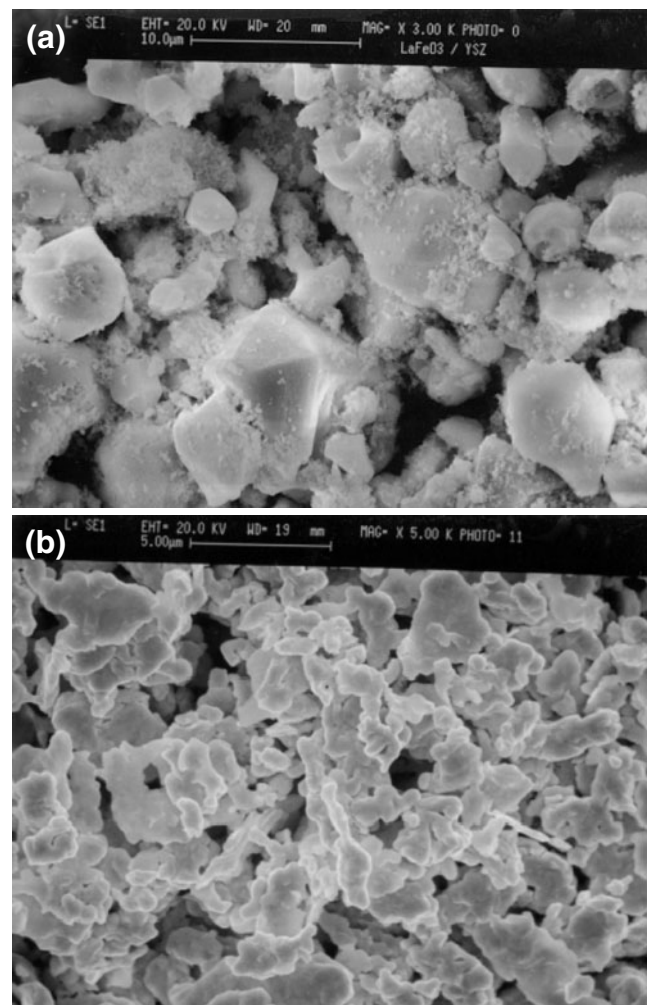

Fig. 2 (**a**) SEM images of LaFeO₃ thick films deposited on YSZ after sintering at 750°C for 3 hours. (**b**) SEM images of a Pt electrode deposited on YSZ after sintering at 750°C for 10 min

of semiconducting oxide and Pt electrodes, both as-prepared and after gas exposure.

Table 1 XPS Binding energies (eV) of the surface of LaFeO₃ electrodes before and after exposure to NO₂

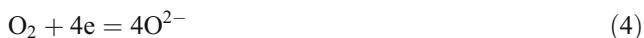|	Nitrogen (N 1s)	Oxygen (O 1s)			Iron (Fe 2p)		Lantanium(La 3d)	
		O_1	O_2	O_3	$2p_{3/2}$	$2p_{1/2}$	$3d_{3/2}$	$3d_{1/2}$
After exposure to NO₂	406.9	527.9	529.1	531.2	710.3	723.8	833.8	851.6
Before exposure to NO₂	–	527.7	529.2	531.1	710.0	723.5	833.6	851.4

O_1 lattice oxygen, O_2 oxygen adjacent to anion vacancy or adsorbed oxygen O_2^{2-}, O_3 hydroxyl group oxygen or adsorbed water

reactions occur at the three-phase boundary between the solid electrolyte, electrode and gas:

for NO₂,

$$NO_2 + 2e = NO + O^{2-} \tag{1}$$

$$2O^{2-} = O_2 + 4e \tag{2}$$

for CO,

$$CO + O^{2-} = CO_2 + 2e \tag{3}$$

$$O_2 + 4e = 4O^{2-} \tag{4}$$

According to mixed potential theory, the above reactions take place at the sensing electrode with the metal oxide. However, both reactions occur at both electrodes in the case of sensors with both electrodes are exposed to the same gas. Therefore, the EMF results cannot be explained by electrochemical reactions at the three phase boundary. In particular, the electrochemical reaction (1) that should occur mainly at the oxide sensing electrode cannot account for the negative EMF values of the p-type semiconducting oxide-based sensors in the presence of NO₂ gas. Thus, the adsorption mechanism appears to be predominant. Indeed, the change in EMF is compatible
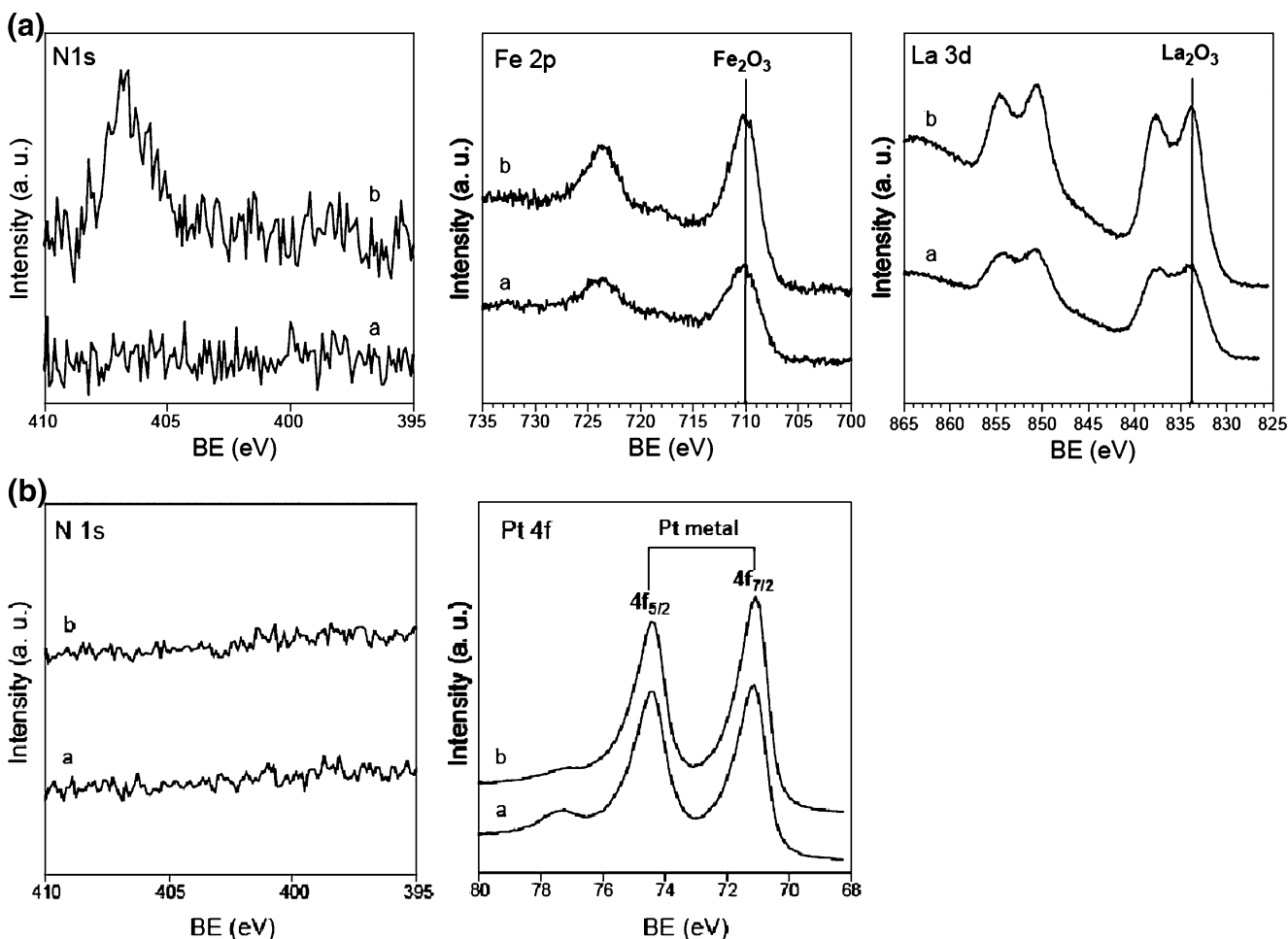

Fig. 3 (a) N1s, Fe 2p and La 3d XPS peaks of the LaFeO₃ thick electrode as prepared **a** and after NO₂ exposure **b**. (b) N 1 s and Pt 4f XPS peaks of the Pt electrode as prepared **a** and after NO₂ exposure **b**

with the changes in resistance induced by the chemisorption of an oxidizing or reducing gas on n- or p-type semiconductors. The results in Fig. 1(a) and Fig. 1(b) are in agreement with adsorption of reducing (CO) and oxidising (NO$_2$) gases on the sensing oxide surface, suggesting that chemisorption plays a major role in the gas sensing mechanism.

Figure 2(a) presents SEM images of the surface morphology of the LaFeO$_3$ thick films on YSZ after sintering at 750°C for 3 h. The sintered LaFeO$_3$ consisted of a porous structure with large grains ranging in size from 2 to 10 μm. The LaFeO$_3$ grains consist of homogeneous nano-sized particles approximately 50 nm in size. Figure 2(b) shows a typical SEM image of the Pt electrode deposited on a YSZ pellet. High porosity and plate-like grains can be observed.

XPS was carried out to determine the chemical state and composition of the sensors before and after exposure to 1000 ppm of NO$_2$ in air. Table 1 lists the binding energies of LaFeO$_3$ and Pt electrodes. Figure 3(a) shows the N 1 s, Fe 2p and La 3d XPS peaks of the LaFeO$_3$ thick electrode as prepared (a) and after NO$_2$ exposure (b). No significant changes in the binding energy were observed for either La 3d or Fe 2p. The binding energies of La 3d$_{5/2}$ and Fe 2p$_{3/2}$ were 833.7 eV and 710.0 eV, respectively. The BE of La 3d and Fe 2p were similar to those of La$_2$O$_3$ and Fe$_2$O$_3$ [18], which were independent of NO$_2$ exposure. A nitrogen peak was observed only on the electrode exposed to NO$_2$ atmosphere. The peak position of nitrogen was observed at 406.9 eV, which corresponds to nitrates, i.e., M(NO$_3$)$_x$, where M is a transition metal [18]. As shown in Fig. 3(b), the Pt 4f$_{7/2}$ binding energies in the Pt electrodes were almost constant at 71.0 eV [18] indicating that Pt electrodes are in the metallic state both with and without NO$_2$ exposure. Moreover, no nitrogen peak was detected, even when the Pt electrode was exposed to NO$_2$. Therefore, only NO$_2$ gas was adsorbed on the LaFeO$_3$ electrodes. The adsorption of NO$_2$ on LaFeO$_3$ can be understood by considering the interactions between NO$_2$ and the surface of the p-type semiconductor. The adsorption of oxidizing gases reduces the number of free electrons in the material and increases the hole concentration. This behaviour was well documented in a previous report [19], i.e. the electrical conductivity of p-type LMO$_3$ (M=La, Sm) increases in a NO$_2$ atmosphere.

XPS confirmed that the gas sensing mechanism for sensors based on a solid electrolyte coupled with oxide electrodes involves gas adsorption on the semiconducting oxide surface. The adsorption of NO$_2$ occurred only on a LaFeO$_3$ electrode. Mixed potential theory cannot be applied in this case. Therefore, XPS is an attractive tool for examining the NO$_2$ sensing mechanism for non-Nernstian sensors.

4 Conclusions

XPS of LaFeO$_3$-based sensors showed a peak of bonded nitrogen due to the adsorption of NO$_2$ on the semiconducting oxide electrode surface when exposed to NO$_2$ gas. This confirms the hypothesis that the adsorption-desorption behaviour and characteristics of semiconducting oxides affects the gas-sensitive EMF response of non-Nernstian sensors.

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