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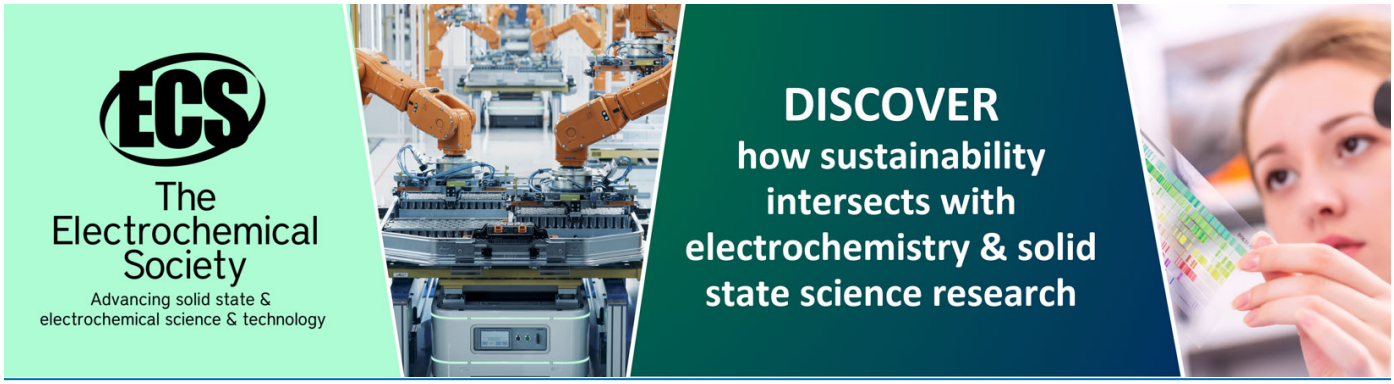

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Effects of Sr Addition to La-Based Perovskite Sensing-Electrode on YSZ-Based Amperometric-Type NOx Sensor

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Abstract. Sensing characteristics of amperometric NOx sensor using yttria-stabilized zirconia (YSZ) and La-based perovskite-type oxide sensing-electrode (SE) was examined. $La_{0.8}Sr_{0.2}MO_3$(M=Co, Mn, Fe) and $LaMnO_3$ was synthesized by means of spray pyrolysis method. The sensor attached with $La_{0.8}Sr_{0.2}MnO_3$ as a SE showed the highest occupancy rate of NO_2 response in total current as well as low current response to CO, C_3H_6, NH_3 at 600°C in O_2 (21%). The response was increased with increasing NO_2 concentration in the examined range between 50 to 800 ppm. The comparison of sensing property between $LaMnO_3$-SE and $La_{0.8}Sr_{0.2}MnO_3$-SE showed the substitution Sr for La improved the NO_2 response for the sensors.

1. Introduction

At present, lean-burn type engines or diesel engines for passenger cars have been developed and installed into automobiles to improve fuel efficiency. In addition, the treatment of NOx emitted from these engines is thought to be difficult to clear the latest emission regulations. Thus, NOx storage catalyst or selective catalytic reduction (SCR) system and inexpensive NOx sensors which respond selectively, quickly, and quantitatively are necessary.

In regard to NOx sensor, zirconia-based type is one of the potential candidates because of mechanical and chemical stability of YSZ even at high temperature and many studies have been examined and reported [1-7]. We have focused on La-based perovskite oxides as SEs for YSZ-based sensor, because these oxides have a property to decompose NO. Until now, in our group, the sensing characteristics of the YSZ-based amperometric NOx sensor attached with $La_{0.6}Sr_{0.4}Co_{0.98}Mn_{0.02}$-SE were examined and reported the sensor showed high sensitivity and selectivity to NOx [8]. And also, the valence variation of transition metal in La-based perovskite plays an important role for this catalytic property [9]. In this study, sensing performances of the amperometric NOx sensors using La-based perovskite oxide-SEs containing Co, Mn, Fe were examined, and the effects of Sr addition to La-based perovskite oxide for the sensor were discussed.

2. Experimental

The perovskite oxides were prepared by spray pyrolysis method. The precursor solutions were made from $La(NO_3)_3{\cdot}6H_2O$ (99.9%, Wako), $Sr(NO_3)_2$ (98%, Kanto Chemical) and each of $Co(NO_3)_2{\cdot}6H_2O$ (99.5%, Wako), $Mn(NO_3)_2{\cdot}6H_2O$ (99.9%, Wako), $Fe(NO_3)_3{\cdot}9H_2O$ (99.9%, Wako). Each of these solutions was misted ultrasonically and introduced to the tubular furnace kept at 800°C with air flowing, and calcined at 800°C for 2h in air. The obtained products were characterized by X-ray

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diffractometry (XRD, RINT 2000) using Cu-Kα radiation and scanning electron microscopy (SEM, S-4500, Hitachi). The adsorption-desorption behaviour of NO for the oxide powders was examined by using a temperature-programmed desorption (TPD) apparatus (TPD type R, Rigaku). The each of oxide powders was treated with 5000 ppm NO diluted in He at R.T. for NO adsorption and then heated up to 800°C at the rate of 5°C/min using mass spectrometer as a detector.

The each of obtained powders was thoroughly mixed with α-terpineol in the weight ratio of 1:1 and screen-printed on one side of YSZ pellet (ϕ=9 mm, t=1.5 mm) as a SE. In addition, the pure Pt paste was also screen-printed on the other side of YSZ pellet to form a counter electrode (CE). Then the sensor element was attached to magnesia tube with inorganic adhesive. The fabricated sensor was assembled in a quartz tube and the sensing characteristics were measured using a conventional gas-flow apparatus equipped with a furnace operating in the temperature range of 400–650°C. The total flow rate of the base gas (dry synthetic air) or the sample gas was fixed at 100 cm^3/min. The sample gases were prepared by diluting the parent gases with dry synthetic air. Reaction curves of the sensor were measured using a potentiostat (Solartron-1287) with two-electrode setup.

3. Results and discussion

Figure 1 shows XRD diffraction patterns of La-based perovskite oxides ($LaMnO_3$ and $La_{0.8}Sr_{0.2}MO_3$, M=Co, Mn, Fe). The each of oxides was characterized as a perovskite structure, namely, $LaMnO_3$(LM), $La_{0.8}Sr_{0.2}CoO_3$ (LSC), $La_{0.8}Sr_{0.2}MnO_3$ (LSM), $La_{0.8}Sr_{0.2}FeO_3$ (LSF), respectively. Grain's shape of oxides except in the LSC was sphere, while the LSC powder has irregular surfaces. All of oxides had various grain size ca 0.3–1μm.

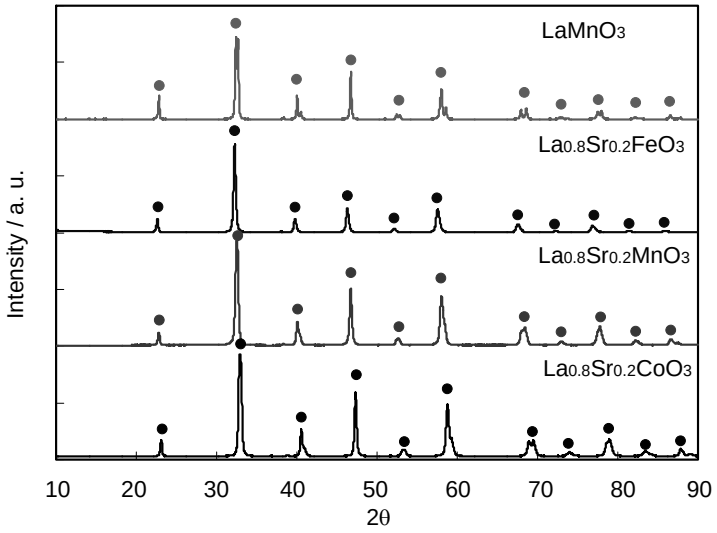

Figure1 XRD patterns of the La-based oxide powders prepared by spray pyrolysis.

Figure 2 shows the comparison of the current values to base gas and 500 ppm NO_2 of the sensors using the three kinds of oxide-SE at applied potential of -50 mV (vs. Pt-CE) as well as the occupancy rate of NO_2 response ($I_{NO2} - I_{base}$) in total current (I_{NO2}) as a rhombus shape. In this figure, LSM-SE and LSF-SE showed the high NO_2 response, and LSM-SE showed lower base current than LSF-SE. LSM-SE also showed the highest occupancy rate of NO_2 response in total current. These facts mean the sensor using LSM-SE has a possibility detecting low concentration of NO_2 even in the excess of O_2. Thus, LSM was chosen as the appropriate material in this study.

To choose optimum operation temperature, the current responses of the sensor to base gas and the 500 ppm NO_2 were measured at 400, 450, 500, 550, 600, 650°C. Although the sensitivity was the lowest to NO_2 at 400°C, the high occupancy rate of NO_2 response in total current was observed. Increasing the operating temperature, the ratio of NO_2 response in total was decreased and current value to NO_2 was increased. Thus, considering these two factors, the optimum operation temperature

was considered to be 500°C. Response properties to NO_2, CO, C_3H_6, NH_3 (500 ppm each) of the sensor at 500°C were examined. The current value to NO_2 was high, although the base current was low and the current values to CO, C_3H_6, NH_3 were almost same with base current. Thus, this sensor showed selectivity to NO_2. We have also confirmed the NO_2 response was increased with increasing the concentration of NO_2 between 50 to 800 ppm at 500°C.

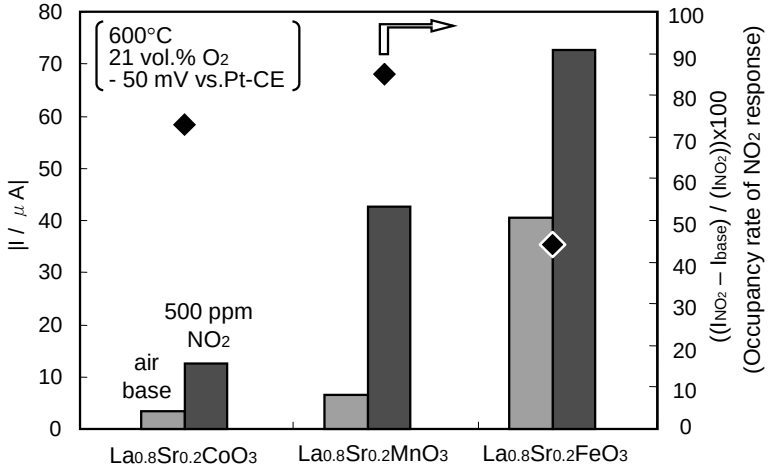

Figure2 Comparison of response current to base gas and 500 ppm NO_2 as well as the occupancy of NO_2 sensitivity in total (♦) of the sensor using La-based perovskite oxides at 600°C.

In order to understand the effect of Sr addition to La-based perovskite oxide for the sensor, response current to base gas and 500 ppm NO_2 for the sensor using LM-SE as a SE was examined. Figure 3 shows the comparison of current values between LM-SE and LSM-SE to base gas and 500 ppm NO_2 at 500°C. The current value to 500 ppm NO_2 of the sensor using LSM-SE was normalized as 1. The current value to NO_2 of the sensor using Sr containing perovskite was more than two times higher than the one using LM-SE although both sensors showed almost same base current. Therefore we have found Sr addition to La-based perovskite increases an effect to NO_2 detection for the sensor.

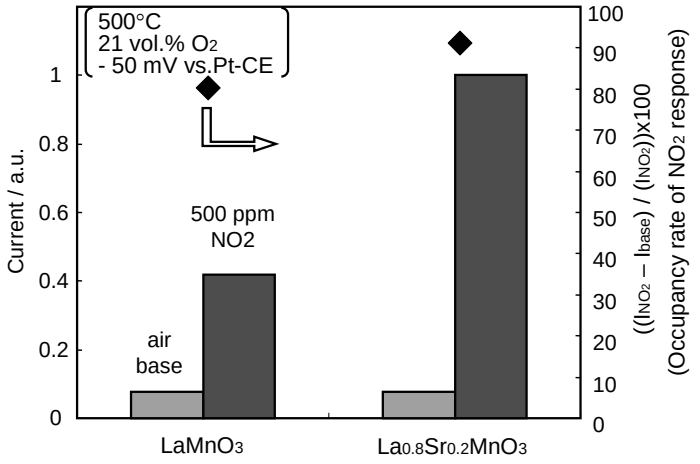

Figure3 Comparison of response current to base gas and 500 ppm NO_2 as well as the occupancy of NO_2 sensitivity in total (•) of the sensor using $LaMnO_3$, $La_{0.8}Sr_{0.2}MnO_3$.

Adsorption-desorption behaviour of NO for the LM and LSM were examined for analyzing the difference of sensing properties of these sensors. Figure 4 shows TPD profiles of m/z=30 for these powders. In the case of LM, two desorption peaks were observed approximately at 120 and 200°C. On the other hand, in the case of LSM, three desorption peaks were observed at 120, 200, 450°C. The desorption peak at high temperature of 450°C which measured only in LSM powder is thought to

bring the difference of sensing property between them. In general, the higher desorption temperature, the higher NO adsorption ability on the surface. The operation temperature of the sensor was mainly 500 or 600°C in this paper. We regard the improvement of NO adsorption has a connection with the increase of sensing property of our sensors.

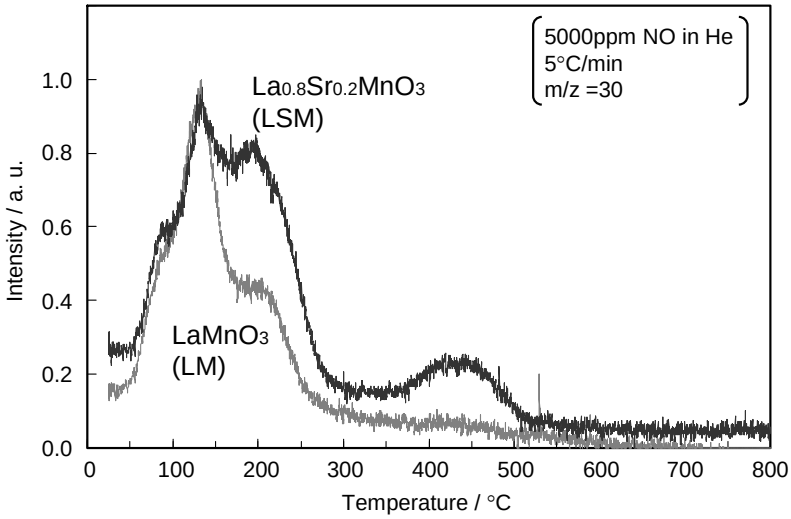

Figure4 TPD profiles of $LaMnO_3$ and $La_{0.8}Sr_{0.2}MnO_3$ powder in the temperature range of 25-800°C

4. Conclusion

Four kinds of La-based perovskite-type oxides, $La_{0.8}Sr_{0.2}MO_3$ (M=Co, Mn, Fe) and $LaMnO_3$ was synthesized by means of spray pyrolysis method. The obtained powders were characterized as a perovskite structure. The sensor attached with $La_{0.8}Sr_{0.2}MnO_3$ showed the highest occupancy rate of NO_2 response in total current as well as selective response. The NO_2 response was increased with increasing NO_2 concentration in the examined range of 50 to 800 ppm. The NO_2 response of $La_{0.8}Sr_{0.2}MnO_3$-SE was higher than the one of $LaMnO_3$-SE. The substitution Sr for La enhanced adsorption property of NO on the La-based perovskite oxide.

Acknowledgements

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