Sol-Gel Synthesis of Perovskite-Type Oxide Thin-Film Using Metal Organic Acid and Its Application to Amperometric Hydrogen-Phosphate Ion Sensor

Keiko Tsuchida, Satoko Takase and Youichi Shimizu*

Department of Applied Chemistry, Faculty of Engineering, Kyushu Institute of Technology,
Sensui-cho, Tobata, Kitakyushu 804-8550, Japan

The synthesis of La-based perovskite-type oxide ($LaBO_3$: B = V, Mn, Fe, Co, Ni) thin-films by a sol-gel method using metal organic acids, and their amperometric sensing properties for hydrogen-phosphate ions were investigated. La-based perovskite-type oxide thin-films could be easily synthesized at 600–700°C on Au-coated alumina substrates. Particularly, the $LaCoO_3$ thin-film prepared at 700°C showed good amperometric responses to HPO_4^{2-} at a concentration between 1.0×10^{-6} and 1.0×10^{-2} M with a sensitivity of 20 $mA \cdot cm^{-2} M^{-1}$, when the applied potential was +1.0 V vs. SCE at 30°C. The 90% response time of the sensor device was as short as approximately 3 min, and showed a high selectivity to HPO_4^{2-} among the examined anions of NO_3^-, Cl^- and SCN^-.

1.   Introduction

La-based perovskite-type oxides containing transition metals, such as $LaBO_3$ (B: transition metal), are well-known as functional inorganic materials having a wide range of applications for electrode materials in the solid oxide fuel cell (SOFC),[1] metal-air battery,[2] gas sensor,[3] ion sensor,[4] and for high-performance catalysts[5] for the complete oxidation of hydrocarbons or CO, and NO reduction. To date, oxide thin-films with a perovskite-type structure for functional electrochemical devices have been prepared by dry processes, such as sputtering and electron-beam deposition methods, as well as the wet

---

*Corresponding author, e-mail address: shims@che.kyutech.ac.jp

processes of the sol-gel method mainly starting from metal alkoxides or organic acid salts.[6–9] They can yield high-quality oxide thin-films, however, they still have some problems, such as relatively low cost performance and the difficulty of handling the chemicals used by the sol-gel method. Among the available techniques, the metal organic-acid method developed by Mizuta *et al*.[6,7] seems to be one of the most promising methods for fabricating La-based perovskite-type oxide thin-films from the viewpoint of its low cost and the ease of preparation of the starting materials. However, the preparation conditions as well as the characteristics of the products have not been clarified.

In this work, we have studied the preparation process of La-based perovskite-type oxide thin-films. It was found that $LaBO_3$ (B= V, Mn, Fe, Co, Ni) thin-films could be prepared on Au-coated alumina substrates using metal organic acids at 600–700°C under pure oxygen flow. The various perovskite-type oxide thin-films obtained were also studied for application as amperometric hydrogen-phosphate ion sensors,[10] which should be applicable to environmental monitoring, as well as in the field of many manufacturing processes. It was revealed that the magnitudes of the sensing currents at a potential of +1.0 V vs. SCE was in the order $LaCoO_3 \gg LaMnO_3 > LaNiO_3 = LaFeO_3 > LaVO_3$.

We report here on the synthesis conditions of La-based perovskite-type oxide thin-films using metal organic acids and their application to hydrogen-phosphate ion sensors.

2.   Materials and methods

Perovskite-type oxide thin-film electrodes ($LaBO_3$: B= V, Mn, Fe, Co, Ni) were prepared by the wet-chemical process using metal organic acids on an alumina substrate with an Au electrode as shown in Fig. 1. Mixtures of the solutions of the reagents of metal
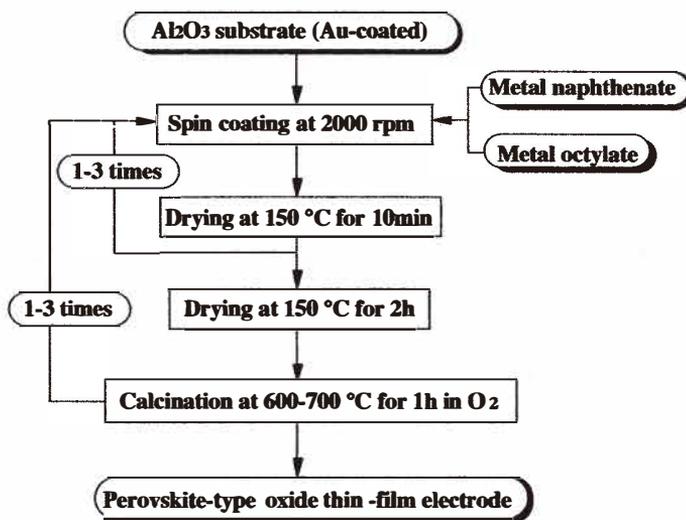
Fig. 1.   Preparation procedure for perovskite-type oxide thin-film.

organic acids (La–, Fe–, V– naphthenates; or Mn–, Co– octates: Soekawa Chemical, Kishida Chemical; metal-contents: 2–8 wt%) with toluene (0–50 wt%) in the proportion of the desired perovskite-type oxide were spin-coated onto Au-coated alumina substrates (10×10×1 mm^t) at 2000rpm, dried at 150°C for 2 h and calcined at 600–700°C under pure oxygen flow. Au-coating on the alumina substrates was performed by a sputtering method (JFC-1100, JEOL). The processes of spin-coating and calcination was repeated 1–3 times. The products were characterized by methods such as X-ray diffraction (XRD) (JDX-3500K, JEOL) using Cu-K$_{\alpha 1}$ radiation and scanning electron microscopy (SEM) (JSM-6320F, JEOL). The amperometric responses of the thin-film electrodes to HPO_4^{2-} were evaluated by the electric current flowing between the oxide thin-film electrodes and the Pt counter electrode under the application of a fixed anodic potential against a saturated calomel reference electrode (SCE) using a potentiostat (Toho Technical Research; PS-14) at 30°C with Ar bubbling. The sample solution was prepared by mixing K_2HPO_4 with a 0.1M H_3BO_3–KOH buffer solution adjusted to be pH 9.2. The effects of NO_3^-, Cl^- and SCN^- were also investigated in the same way using their potassium salts.

3.   Results and Discussion

3.1   *Synthesis conditions of perovskite-type oxide thin-films*

Figure 2 shows the effects of various spin-coating conditions on the formation of a perovskite-type oxide thin-film phase using the metal organic acids for preparing $LaFeO_3$ and $LaCoO_3$ thin-films at 600°C under pure oxygen flow. The formation of the perovskite-type oxide thin-film phase was evaluated by the relative XRD intensity ratios of the (110) line of the perovskite-type oxide phase (I_P) to the (104) line of the alumina phase (I_A) of the substrate. The crystallinity of the perovskite-type oxide thin-film $[I_P /(I_P + I_A)]$ increased with the total amount of spin-coating solution as expected, as shown in Fig. 2(a). The apparent effects of the metal-content of the spin-coating solution or the duration of the spin-coating on the perovskite-type oxide formation were not observed, as shown in Figs. 2(b) and 2(c), respectively. Interestingly, it was found that the amount of solution per spin-coating operation was the most important factor for the synthesis of well-crystallized perovskite-type oxide thin-films. The crystallinity of the perovskite-type phase was a maximum at around 10–15 ml·cm^{-2} / coating, as shown in Fig. 2(d). The reason for this was not clear, however the rheological phenomena during spin-coating seem to be the most important factors in the spin-coating technique. Further investigations to clarify these rheological phenomena are currently in progress.

Figure 3(a) shows the XRD pattern of the $LaCoO_3$ thin-film electrode prepared on an Au-coated alumina substrate at 600°C. Although, small peaks of $La_2O(CO_3)_2$ were observed, a relatively well crystallized hexagonal $LaCoO_3$ perovskite-type oxide thin-film was obtained. $LaBO_3$ (B= Mn, Fe, Co) thin-films were also able to be synthesized by the spin-coating method using metal organic acids at 600°C, while the $LaNiO_3$ thin-films prepared at 600°C included both the perovskite-type oxide phase and an impurity phase of NiO. On the other hand, all the prepared perovskite-type oxide thin-films of $LaBO_3$ (B= V, Mn, Fe, Co, Ni) with almost single phases could be synthesized at the calcination temperature of 700°C under pure oxygen flow by this method, as shown in Fig. 3(b) and
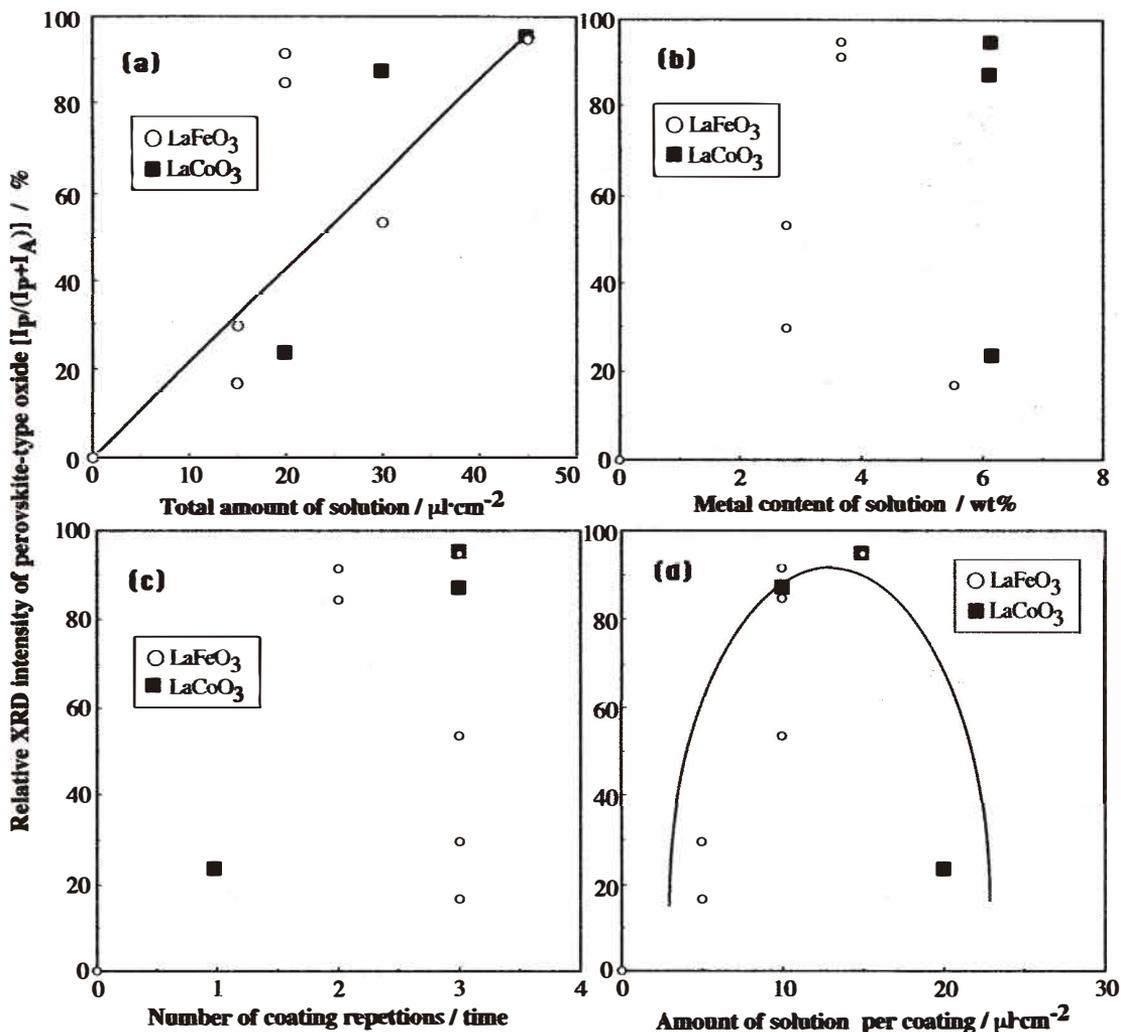
Fig. 2. Effects of the spin-coating conditions on the formation of perovskite-type oxide thin-film after sintering at 600°C. (a) Effect of total amount of spin-coating solution, (b) Effect of metal-content in spin-coating solution, (c) Effect of the number of spin-coating repetitions (d) Effect of the amount of spin-coating solution used for each spin-coating step. I_P: XRD intensity of (110) line of perovskite-type oxide; I_A: XRD intensity of (110) line of alumina substrate.

Fig. 4. The reflections of $LaCoO_3$, $LaMnO_3$, $LaNiO_3$, $LaFeO_3$ and $LaVO_3$ were consistent with reported values (JCPDS, 9–358, 35–1353, 34–1181, 15–148, and 36–141, respec-tively). The difference between the $LaVO_3$ thin-film structure and that of the other thin-
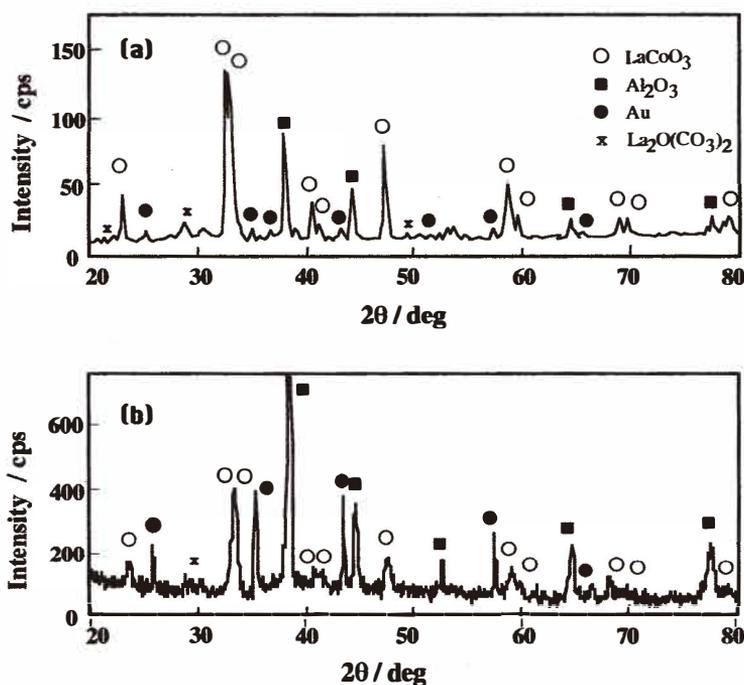
Fig. 3.   XRD pattern of the LaCoO₃ thin-film prepared on an Au-coated alumina substrate at 600°C (a) and 700°C (b).

films came from the difference in the orthorhombic systems, i.e., the lattice constants (a, b, c) of the $LaVO_3$ largely differed, compared with the other perovskite-type oxide systems which showed tetragonal-like structures (a b).

The SEM image of the $LaCoO_3$ thin-film prepared at 700°C revealed that the surface of the film was relatively smooth and consisted of the homogeneous fine grains of dimension approximately 20 nm, as shown in Fig. 5, and the thickness of the thin-film was approximately 500 nm.

3.2   *Amperometric ion sensing properties*

As the perovskite-type oxide thin-films prepared at 700°C showed better sensing properties than the films prepared at 600°C, thereafter, the perovskite-type oxide thin-films prepared at 700°C were applied to the sensor devices

Figure 6 shows the cyclic voltammogram (CV) of the $LaCoO_3$ thin-film electrode for various HPO_4^{2-} concentrations at 20 mV/s. The anodic current increased with increasing electrode potential, and the current increased with increasing HPO_4^{2-} concentration above +0.6 V vs. SCE. This suggests that an amperometric sensing of HPO_4^{2-} using anodic current is possible by use of the $LaCoO_3$ thin-film electrode. Under the potentiostatic
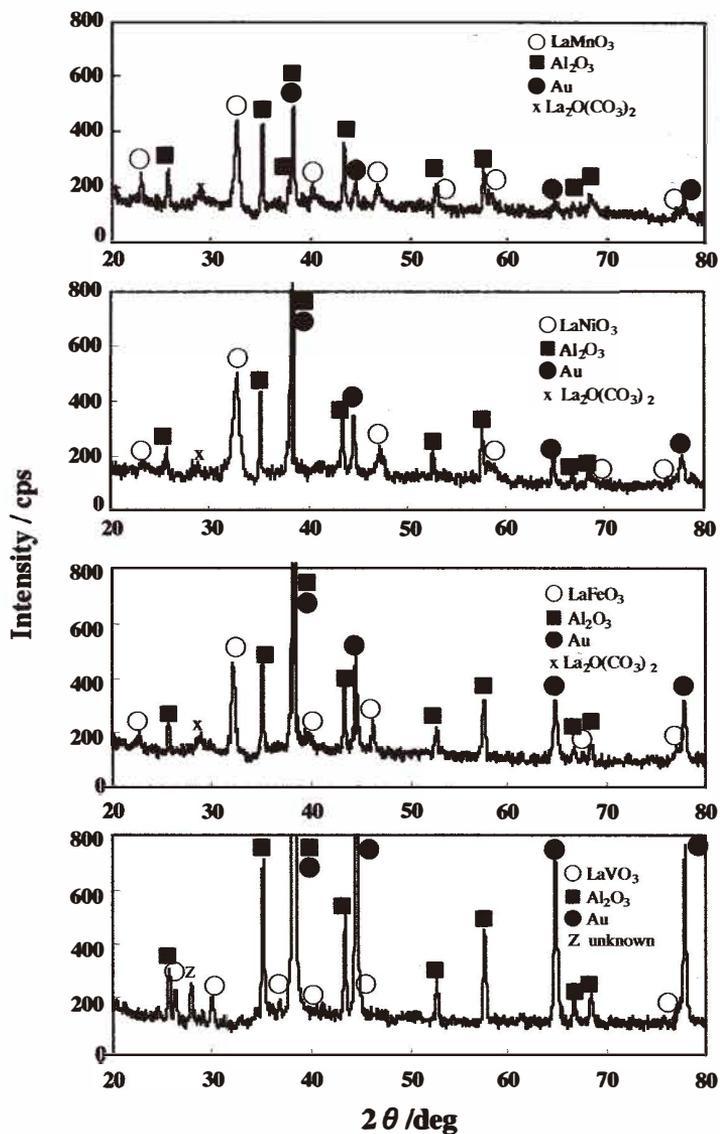
Fig. 4.   XRD patterns of various perovskite-type oxide thin-films prepared on Au coated alumina substrate at 700°C.

condition, the amperometric sensing properties were poor when the potential was lower than +0.8 V vs. SCE, while it was found that a good response was observed at the potential of +1.0 V vs. SCE. The higher overpotential observed for the sensor is considered to come from the difference between the dynamic (CV) and static sensing conditions. The ion-
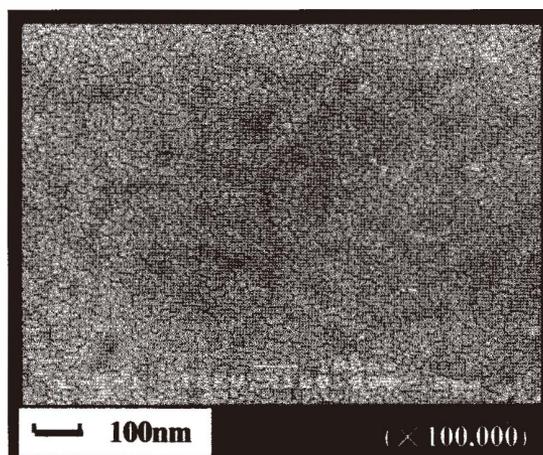
Fig. 5.   SEM photograph of the surface of the LaCoO₃- thin-film prepared at 700°C.
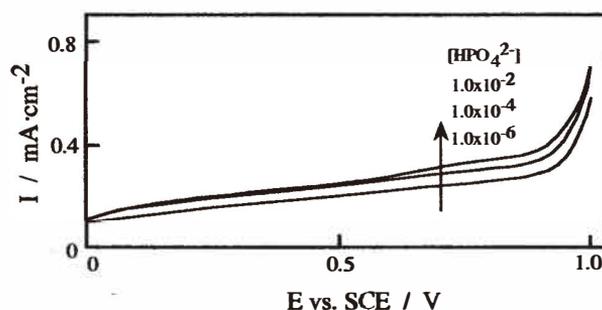
Fig. 6.   I-V characteristics of the LaCoO₃ thin-film electrode prepared at 700°C for various concentration of HPO_4^{2-} at 30°C. (Supporting electrolyte: 0.1 M H_3BO_3/KOH, pH = 9.2, Ar bubbling. Scanning rate: 20 mV/s)

diffusion polarization has much influence upon the overpotential. Figure 7 shows the change in the current density of the LaCoO₃ thin-film sensor element with changing HPO_4^{2-} concentration at 1.0 V vs. SCE. The apparent response was observed at a concentration greater than 1.0×10^{-6} M. The sensing current increased with increasing HPO_4^{2-} concentration between 1.0×10^{-6} and 1.0×10^{-2} M. The 90% response time from 1.0×10^{-4} to 1.0×10^{-3} M was approximately 3 min at 30°C.

The performance at sensing the hydrogen-phosphate ions of the various perovskite-type oxide thin-films ($LaBO_3$; B = Mn, Fe, Co, Ni, V) is also shown in Fig. 7. Particularly, the LaCoO₃ system was found to show the highest sensitivity to HPO_4^{2-} among the examined oxides as also shown in Fig. 7. The magnitudes of the sensing currents at a potential of +1.0 V vs. SCE was in the order $LaCoO_3 \gg LaMnO_3 > LaNiO_3 = LaFeO_3 >$
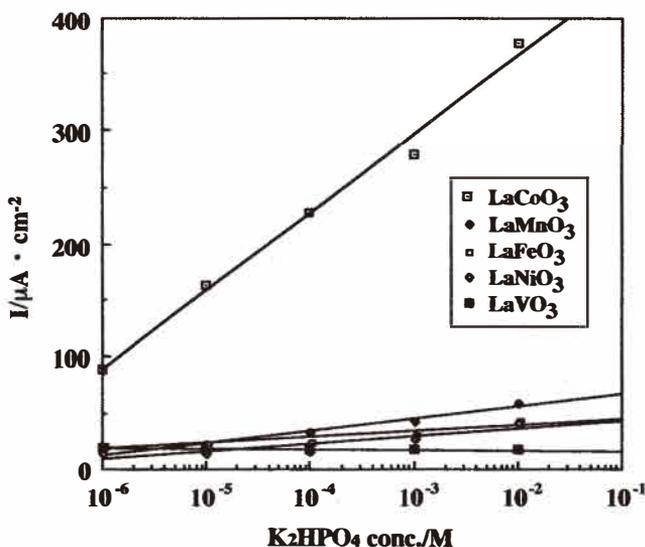
Fig. 7.   Response characteristics of the thin-film devices to K_2HPO_4 at 30°C. (E: 1.0 V vs. SCE; calcination temperature: 700°C; supporting electrolyte: 0.1 M H_3BO_3/KOH, pH = 9.2, Ar bubbling).

$LaVO_3$, however the $LaVO_3$ and $LaFeO_3$ systems showed poor response characteristics. The increase in overpotential from +1.0 to +2.0 vs. SCE gave no improvement in the sensing properties of the resistive materials of $LaFeO_3$ and $LaVO_3$, and they showed almost the same background current as those of the $LaBO_3$ thin films (B = Mn, Ni). Thus, the resistance of the perovskite-type oxide thin-films did not influence amperometric sensing in this study. In addition, no response was observed using only the Au-electrode, so the exposed Au on the oxide thin-film electrode had no effect on amperometric sensing. As the Co_3O_4 thin-film prepared by the same wet-process had no sensitivity to HPO_4^{2-}, the perovskite-type phase seems to play an important role in the amperometric sensing of HPO_4^{2-}.

The sensitivity of the $LaCoO_3$ thin-film electrode at close range to the other common anions, such as NO_3^-, Cl^-, and SCN^- was further investigated. As shown in Fig. 8, the $LaCoO_3$ element showed some anodic current to in response to the presence of SCN^-, NO_3^- and Cl^-, however the current was not dependent on the change in the concentrations of these anions. The $LaCoO_3^-$ based element had a high sensitivity of 20 mA $\cdot$ cm^{-2}M^{-1} to HPO_4^{2-}, while its sensitivity to SCN^-, NO_3^- and Cl^-, was as small as $-0.1 \sim +3.1$ mA $\cdot$ cm^{-2}M^{-1}.

When the electrode potential of the sensor element is positive, the anodic electrochemical reaction should occur. At an electrode potential of around +1.0 V vs. SCE, electrochemical oxidation of HPO_4^{2-} or other anions was difficult . In those cases, oxygen evolution should take place: ($4OH^- = O_2 + 2H_2O + 4e^-$). Although the anodic reaction
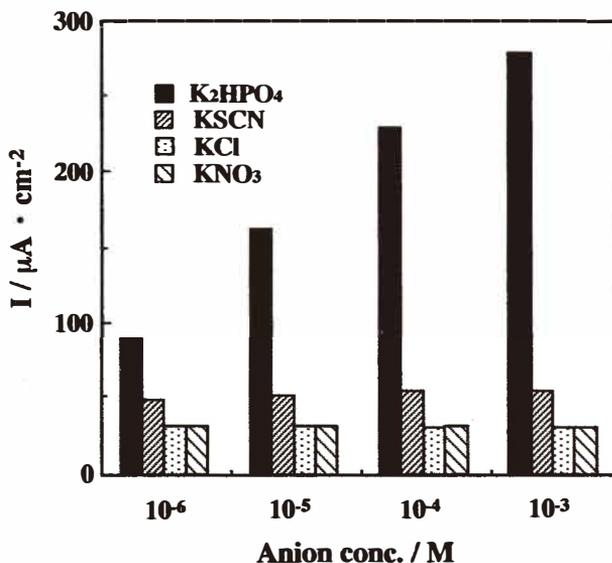
Fig. 8.   Response characteristics to various anions of the LaCoO₃-thin-film device at 30°C. at 1.0 V vs. SCE. (Calcination temperature: 700°C, E: 1.0V vs. SCE; Supporting electrolyte: 0.1 M H_3BO_3/ KOH, pH = 9.2, Ar bubbling)

was largely dependent on the coexisting anions, it was accelerated by the existence of HPO_4^{2-} or some other anions. The sensing current decreased with increasing dissolved oxygen with pure oxygen bubbling into the electrolytes. Although, the mechanism is a hypothesis at this point, the phenomena of the sensing electrode reactions can be tentatively assumed to be that HPO_4^{2-} undergoes the anodic electrode reaction:
($HPO_4^{2-} + 2OH^- = HPO_3^{2-} + O_2 + H_2O + 2e^-$). The difference in magnitude of the sensing currents seems to come from the electrochemical responses of the loaded perovskite-type oxides to the reaction. The quantitative analysis by MASS and ion-chromatography now in progress.

4.   Conclusions

La-based perovskite-type oxide thin-films ($LaBO_3$: B = V, Mn, Fe, Co, Ni) were able to be synthesized by a sol-gel method using metal organic acids at 600–700°C. The spin-coating conditions were found to play a very important role in the preparation of well-crystallined perovskite-type oxide thin-films. The $LaCoO_3$ thin-film type sensor device synthesized at 700°C responded to HPO_4^{2-} between 1.0×10^{-6} and 1.0×10^{-2} M. The $LaCoO_3$ thin-film sensor device showed the highest selectivity to HPO_4^{2-} among the examined anions.

Acknowledgment

References

1   O. Yamamoto, Y. Takeda, R. Kanno and M. Noda: Solid State Ionics **22** (1987) 241.
2   Y. Shimizu, K. Uemura, N. Miura and N. Yamazoe: Chem. Lett. **1988** (1988) 1979.
3   H. Obayashi, Y. Sakurai and T. Gejo: J. Solid State Chem. **17** (1976) 199.
4   Y. Shimizu, H. Komatsu, S. Michishita, N. Miura and N. Yamazoe: Sensors and Actuators B **34** (1996) 493.
5   M. Skoglundh, L. Löwendahl, K. Jansson, L. Dahl and M. Nygren: Appl. Catal. B. **3** (1994) 259.
6   T. Kumagai, H. Yokota, K. Kawaguchi, W. Kondo and S. Mizuta: Chem. Lett. (1987) 1945.
7   T. Kumagai, H. Yokota, K. Kawaguchi, W. Kondo and S. Mizuta: Denki Kagaku (presently Electrochemistry) **55** (1987) 269.
8   H. J. Hwang and M. Awano: J. Euro. Ceram. Soc. **21** (2001) 2103.
9   R. N. Singh, S. K. Tiwari, S. P. Singh, N. K. Singh and G. Poillerat: J. Chem. Soc. Fraday Trans. **92** (1996) 2593.
10 Y. Shimizu, A. Ishikawa, K. Iseki and S. Takase: J. Electrochem. Soc. **147** (2000) 3931.