Amperometric Sensor For Hydrogen-Phosphate Ion With Perovskite-Type Oxide Thin-Film

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ABSTRACT

Amperometric hydrogen-phosphate ion sensor based on perovskite-type oxide ($La_{1-x}A'_xBO_3$: A'= Ca, Sr, Ba, Ce, B= Cr, V, Mn, Fe, Co, Ni : x = 0~0.2) thin-films synthesized by an polymeric precursor method was investigated. Especially $La_{1-x}A'_xCoO_3$ systems obtained at 450~500°C from metal nitrates, polymer and organic additives on an ITO- glass substrate showed good amperometric responses to HPO_4^{2-} at the concentration between $5.0x10^{-5}$~$1.0x10^{-3}$M. This sensor element showed high selectivity to HPO_4^{2-} among the examined anions of NO_3^-, Cl^-, and SCN^-.

INTRODUCTION

It has been becoming very important for hydrogen-phosphate ion measurement for agriculture, clinical medicine, and environmental protection. So far, many kinds of hydrogen-phosphate ion sensors, such as ion selective electrodes[1], bio-related systems [2] have been reported. We have been investigated a hydrogen-phosphate ion sensor based on electrochemical reactions of various electrode materials. Recently, we have found that La-based perovskite-type oxides thin-film electrodes showed good properties of amperometric sensing to hydrogen-phosphate ion[3]. We report here novel synthesis technique of the La-based perovskite-type oxide thin-film electrodes as well as their hydrogen-phosphate ion sensing properties.

EXPERIMENTAL

Perovskite-type oxide($La_{1-x}A'_xBO_3$: A'=Ca,Sr,Ba,Ce, B= V,Cr,Mn,Fe,Co,Ni: x=0~0.2) thin-films were prepared by various wet-chemical processes on an Au-coated alumina (ITO-glass) substrate using mixed organometallic solutions or a polymeric precursor using metal nitrates, acetylacetone, and polyvinylalchol or polyvinylpyrrolidone. The obtained solutions were spin-coated on the substrate dried and calcined at 500~800 ℃.

The amperometric responses of thin-film electrodes to HPO_4^{2-} were evaluated by the electric current flowing between the oxide thin-film electrodes and Pt counter electrode under applying a fixed anodic potential against an SCE by using a potentiostat at 30℃. The effects of NO_3^-, Cl^-, SCN^- were also investigated in the same way using their potassium salts.

RESULTS AND DISCUSSION

Preparation of perovskite-type oxide thin-film

The $LaBO_3$ (B= V, Mn, Fe, Co, Ni) thin-film were able to synthesize by the sol-gel method using mixed organometallic solutions at 600℃, but no $LaCrO_3$ was synthesized by this method. On the other hand, the various perovskite-type oxides could be obtained by an polymer precursor method. Almost all oxides could be obtained at 600-800 ℃. Furthermore $La_{0.8}A'_{0.2}CoO_3$(A'= Ca, Sr, Ba, Ce) thin-film electrode could be prepared on a glass substrate with ITO at 500℃ as well as $LaCoO_3$ thin-film. Thickness of the thin-films was ranged between 200 and 500nm. XRD pattern of the prepared thin-film showed well-crystallized and almost single phase perovskite-type oxide.

Hydrogen phosphate ion sensing properties

Among the $LaBO_3$ (B= V, Cr, Mn, Fe, Co, Ni) electrode systems, the $LaCoO_3$- and $LaMnO_3$- based elements showed amperometric responses to HPO_4^{2-} at +1.0V vs. SCE. Especially, the $LaCoO_3$ system was found to show the highest sensitivity to HPO_4^{2-} at the concentration between $1.0x10^{-5}$~$1.0x10^{-3}$M, with the 90% response time to $1.0x10^{-3}$M HPO_4^{2-} of ca. 3min. In addition, this sensor element showed remarkable selectivity to HPO_4^{2-} among the anions of NO_3^-, Cl^-, and SCN^-. It was further found that the use of $La_{0.8}A'_{0.2}CoO_3$ (A'= Ca, Sr, Ba, Ce) systems as the electrode materials gave higher stability than that of the non-doped $LaCoO_3$ system for the amperometric sensing. From the results it appeared to $La_{0.8}Sr_{0.2}CoO_3$ based element showed the highest sensitivity to HPO_4^{2-}. Furthermore the $La_{0.8}Sr_{0.2}CoO_3$ thin-film electrode showed remarkable selectivity to HPO_4^{2-} among the examined NO_3^-, Cl^-, SCN^- (Fig. 1).

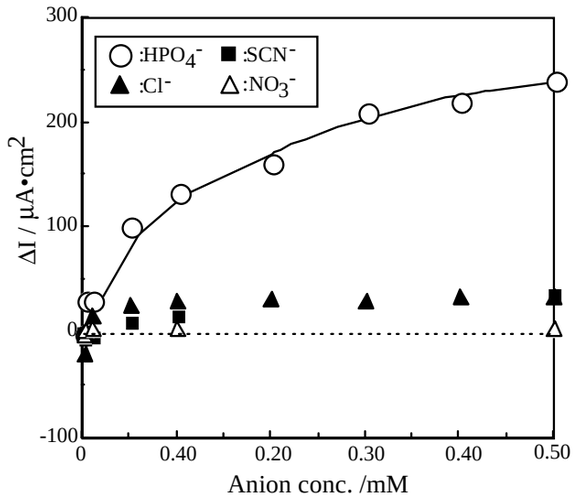

Fig. 1 Sensing performance of $La_{0.8}Sr_{0.2}CoO_3$ thin-film electrode based amperometric hydrogen-phosphate ion sensor

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REFERENCES

[1] E. Punger, K. Toth and J. Haves, *Mikrochim. Acta*., **4**, 689 (1966).
[2] M. Suzuki, H. Kurata, Y. Inoue, H. Shin, I. Kubo, H. Nakamura, K. Ikebukuro and I. Karube, *DENKI KAGAKU*, **66**, 579(1998).
[3] Y. Shimizu, A. Ishikawa, K. Iseki, and S. Takase, *J. Electrochem. Soc*., **147**, 3931 (2001).