Preparation of Amperometric Hydrogen-Phosphate Ion Sensor Based on Perovskite-Type Oxide Thick-Film by EPD Process

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Perovskite-type structured LaCoO$_3$ fine powder with high surface areas could be prepared by a polymer precursor method using acetylacetone (AcAc) as a chelating agent at 500°C. This fine powder could be used for an electrophoretic deposition (EPD) process in an acetylacetone-based suspension. The LaCoO$_3$ fine powder supported on carbon-cross device was prepared by the EPD method without a sintering process. The device showed good properties of amperometric sensing of hydrogen-phosphate ion.

Key Words : Perovskite-type Oxide, Thick-film, EPD, Phosphate Ion Sensor

1 Introduction

An increase in the phosphate ion concentration in a natural water system leads to the eutrophication phenomenon. Consequently, the determination and control of phosphate ion constitutes a priority for water quality. A spectrophotometric method has been widely used for the determination of the phosphate ion concentration, but this method requires sample pretreatment and it is not suitable for the on-site monitoring.

Potentiometric ion selective electrodes have been reported, such as those based on metal,$^1$ and metal complex$^2$ electrodes. However, they suffer from selectivity and poor stability of the sensing materials. Amperometric procedures have been reported for the determination of phosphate as the phosphomolybdate complex.$^3,4)$

Perovskite-type oxides are interesting materials for a wide variety of applications such as catalysts for oxidation, electrodes, electrolytes for fuel cell, chemical sensors,$^5,6)$ and so on. Especially, doped lanthanum cobaltites have high potential applications as catalysts for oxidation and/or reduction reactions. So far, many different sol-gel preparation routes at low temperatures have been developed to obtain perovskite-type oxide fine powders with high surface areas for catalytic applications.$^5,7,8)$ The electrophoretic deposition (EPD) process for preparing thick oxide films, which require for the use of fine powders, have become very attractive for the fabrication of ceramic devices due to the simple technique, low cost, easy control of the ceramic film thickness, and the allows intricate designing.$^7,9)$

The aim of the present work is first to obtain La-based perovskite-type oxide fine powders synthesized by a polymer precursor method,$^{10}$ in which the effects of polymer additives were investigated for low temperature preparation of perovskite-type oxide. Second, the obtained fine powders were used for the fabrication of a perovskite-type thick oxide film device by the EPD process for application of high performance electrochemical sensor devices for the detection of the phosphate ion. We could demonstrated an amperometric hydrogen-phosphate ion sensor, in spite of many kinds of hydrogen-phosphate ion sensors which have already been reported,$^{11,12}$ had not yet used in the practicable applications.

We report the synthesis conditions of La-based perovskite-type oxide fine powders, the conditions for preparing the oxide thick-film by the EPD technique, and the application of the thick-film as an electrochemical hydrogen-phosphate ion sensor.

2 Experimental

The LaCoO$_3$ fine powders were prepared by the polymer precursor (PP) method in the following system$^{10}$ : metal nitrates were dissolved in an ethylene glycol solution at the desired metal molar ratio. Acetylacetone (AcAc) was then added (Oxide: AcAc = 1 mol : 8 mol) as a chelating agent, and then a polymer, i.e., poly(vinyl alcohol) (PVA) or poly (ethylene glycol) (PEG) was added as the polymer additive (7.5 wt %) to form the polymer precursor. The prepared polymer precursors were decomposed on a heating-plate to obtain the powders, which were finally calcined at 300 ~ 600°C for 2 h in air.

The polymer precursors and the obtained perovskite-type oxide powders were characterized by means of X-ray diffractometry (XRD) (JDX-3500K, JEOL) using Cu-K$_{α1}$ radiation, scanning electron microscopy (SEM) (JSD-6320F, JEOL), and differential thermal analysis (TG-DTA)(200, Seiko Instrument, Inc.). The specific surface areas of the oxides were measured by the BET method (Autosorb-1c, Quantachrome).

The obtained fine powders were applied for EPD process to prepare oxide thick-film. The EPD was performed in a glass cell with two electrodes vertically immersed in a suspension of AcAc with the dispersed LaCoO$_3$. An alumina plate with an Au electrode, carbon
paper (TGP-H-060H, Toray), and carbon cloth (GF-20, Nippon Carbon) were used as the working electrode at anode. A Pt-plate counter electrode was used as cathode. The distance of each electrode for the EPD was fixed at 1 cm. The applied voltage was kept constant between +20 V and +40 V using a DC power source (R6243, Advantest).

The amperometric sensing characteristics of the LaCoO₃ supported device for the hydrogen-phosphate ion were evaluated by the electric current flowing between the LaCoO₃ supported electrode and the Pt counter electrode under the application of a fixed anodic potential versus a Ag/AgCl electrode using an electrochemical analyzer (760C, ALS) at room temperature with Ar bubbling. The sample solution was prepared by mixing K₂HPO₄ with a 0.1 M H₂BO₃-KOH buffer solution adjusted at pH 9.2. Cyclic voltammetry experiments were performed using the same system.

3 Results and Discussion

Figure 1 shows the XRD patterns of the LaCoO₃ powders prepared at 200 ~ 500 °C by the PP method with AcAc as the chelating agent and PVA as the polymer additive. Almost only the single-phase perovskite-type oxide was obtained at 500 °C. The other systems included a small impurity phase of La₂O₃CO₃. The LaCoO₃ powder from the AcAc/PVA system showed the high surface area of ca. 24 m²/g.

Figure 2 shows a SEM image of the surface of LaCoO₃ supported on carbon cloth by EPD process from the AcAc-based suspension dispersed with the LaCoO₃ fine powder. The LaCoO₃ was attached tightly to the electrode substrate materials. Sintering process is no necessary for device fabrication as the as-deposited thick film was not removed on the carbon-paper and carbon-cloth, while the LaCoO₃ was easy to remove from the Al-Alumina substrate without sintering at 500 °C after the EPD process.

The cyclic voltammogram (CV) of the carbon-based electrode without the electrocatalyst at various HPO₄²⁻ concentrations showed no electrochemical reactions occurred between −0.50 V and +0.75 V vs. Ag/AgCl, as shown in Fig. 3. On the other hand, the cyclic voltammogram of the LaCoO₃ supported electrode at various HPO₄²⁻ concentrations revealed that the anodic current increased with increasing electrode potential, above +0.67 V vs. Ag/AgCl, as shown in Fig. 4. This suggests that an amperometric sensing of HPO₄²⁻ using an anodic current is possible with the LaCoO₃ electrode. Under the potentiostatic condition, it was found that a good
response was observed at the potential of +0.8 V vs. Ag/AgCl. The higher over potential observed for the sensor should come from the difference between the dynamic (CV) and static sensing conditions. The ion-diffusion polarization had a significant influence on the overpotential. Figure 5 shows the current response of the LaCoO₃/carbon-cloth sensor element changing the HPO₄²⁻ concentration at +0.8 V vs. Ag/AgCl. The apparent response was observed at the concentration above 1.0 × 10⁻¹ M. The sensing current increased with the increasing HPO₄²⁻ concentration between 1.0 × 10⁻¹ and 1.0 × 10⁻² M. The 90% response time from 1.0 × 10⁻¹ M to 1.0 × 10⁻² M was ca. 2 min at 30°C.

The LaCoO₃ system was found to have the highest sensitivity to HPO₄²⁻ among the examined perovskite-type oxides (LaMnO₃ M = Mn, Fe, Co).

When the electrode potential of the sensor element is positive, the anodic electrochemical reaction should occur. At the electrode potential of around +0.8 V vs. Ag/AgCl, the electrochemical oxidation of HPO₄²⁻ occurs. In these cases, oxygen evolution should take place: (4OH⁻ = O₂ + 2H₂O + 4e⁻). Although the anodic reaction was mostly dependent on the coexisting anions, it was accelerated with the existence of HPO₄²⁻ or some anions. The sensing current decreased with the increasing dissolved oxygen due to pure oxygen bubbling into the electrolyte. Although, the mechanism is a hypothesis at this point, the phenomena of the sensing electrode reactions can be tentatively assumed to be that HPO₄²⁻ undergoes the following anodic electrode reaction: (HPO₄²⁻ + 2OH⁻ = HPO₄³⁻ + O₂ + H₂O + 2e⁻).

4 Conclusion

La-based perovskite-type oxide fine powders with high surface areas could be prepared by the polymer precursor method using AcAc and PVA at 500°C. This LaCoO₃ could be supported on a carbon cloth and carbon paper by an EPD method using the AcAc suspension without a sintering process. The LaCoO₃ device responded at the increase of HPO₄²⁻ concentration between 1.0 × 10⁻¹ and 1.0 × 10⁻² M. The LaCoO₃ supported on the carbon cloth sensor device showed the highest sensitivity to HPO₄²⁻ among those examined in this study.

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References


![Fig. 5](image_url)  
Amperometric response characteristics of the LaCoO₃/carbon-cloth device to hydrogen phosphate ion.