Preparation of layered perovskite-type cuprate thick-film electrode by electrophoretic deposition method and its nitrite-ion sensing properties

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Detection of nitrite-ion has become very important for various industrial fields due to its wide application range such as food additives and a rust preventive agent for steels. In this study, we attempted at developing an advanced method to produce layered perovskite-type cuprates based thick-film device for highly sensitive electrochemical sensor for nitrite-ion with a capacity of wide concentration range. Here, layered perovskite-type oxide powders could be synthesized by a polymer precursor method which was deposited on alumina supports with gold electrode by an electrophoretic deposition method. The sensor performance was measured by an amperometric method for nitrite-ion detection. It was found that the Gd₂CuO₄-based electrode showed fast and good linear responses to nitrite-ion for a wide range of concentration.

Key-words : Layered perovskite-type oxide, Gd₂CuO₄, Electrophoretic deposition, Thick-film, Nitrite-ion sensor

Nitrite-ions are widely used as an anti-oxidizer for foods¹²,¹³ and beverages,³ and an important anti-corrosion material for steels.⁴,⁵ It is also well known that NO₂⁻ causes serious eutrophication in closed water systems.⁶ Nitrite-ion itself is toxic⁷ and its permissible concentration range shall be less than micro molar level for drinking water. Then, a quantitative analysis for NO₂⁻ has been become very important in these days. So far, nitrite-ions are usually analyzed by instrumental methods such as UV-vis spectrophotometry⁸,⁹ or ion chromatography,¹⁰ however these techniques require complicated handling process for the measurements and are not suitable for the use at on-site monitoring. Therefore, a compact and simple sensor device has been become very important in these fields.

Until now, the electrochemical NO₂⁻ sensors using nanomaterials,¹¹–¹⁴ metal materials,⁸,¹³ organic complexes¹⁴,¹⁵ polymers,¹² reduced graphene oxide with MnO₂¹⁶ and Fe₃O₄¹⁷ other metal oxide¹⁸ were reported. In these sensors, remarkable interaction between transition metal elements and NO₂⁻ can be seen. These results indicate that transition metal-based mixed oxides are one of the candidate materials for NO₂⁻ sensing. In previous work, we have studied various electrochemical ion sensors for hydrogen-phosphate ion⁹ and hydrogen peroxide²⁰⁺²¹ based on perovskite-type oxides. It was also reported the SmFeO₃ based perovskite-type oxide showed high NO₂⁻ sensing properties.²² However, the response rate of the SmFeO₃ based sensor was rather slow and the NO₂⁻ sensing mechanism on the oxide based sensors is still unclear until now.

In this study, we applied the layered perovskite-type cuprate Ln₂CuO₄ (Ln: Gd, Pr, Sm) as the sensor material²³ as cuprate has unique catalytic characteristics and so far there was no report showing the usage of cuprate as an ion sensor. As the sensor device, Ln₂CuO₄ (Ln: Gd, Pr, Sm) thick-film modified electrodes was prepared by an electrophoretic deposition (EPD) method²⁴,²⁵ to investigate electrochemical properties of NO₂⁻ sensing. It was found that the Gd₂CuO₄ modified electrode showed fast and high NO₂⁻ sensing properties, which should be related to the strength of adsorbed oxygen (Oₐ) on the surface of the Gd₂CuO₄ and redox properties between Cu²⁺ and Cu⁺ in Gd₂CuO₄ should be included in the sensing mechanism.

Layered perovskite-type Ln₂CuO₄ (Ln: Gd, Pr, Sm) oxide powders were synthesized by a polymer precursor method,²⁶,²⁷ i.e., metal (Gd, Pr, Sm, Cu) nitrates of reagent grade were dissolved in 0.50 mol of ethylene glycol, which was mixed with 30 mmol of an acetylacetonate (AcAc) and 7.5 wt% polyvinylpyrrolidone as a coordination agent and a polymer additive, respectively, until a viscous sol was formed. The obtained polymer precursor sols were dried in ambient air to form aerogel powders, which were then heat-treated at 800°C for 2 h. Ln₂CuO₄ modified electrodes were prepared by an EPD method²⁵.

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0.24 g of each oxide powder was suspended in 50 mL AcAc and mixed in a ball mill for 30 min. After the ball-mill treatment, 25 mg I₂ and 50 mL AcAc were added to form EPD electrolyte solution. EPD was carried out using Au-coated Al₂O₃ (Au area: 5 × 10⁻² mm²) as the working electrode and a Pt plate as the counter electrode, respectively. The distance between two electrodes was fixed at 10 mm. After ultrasonic wave treatment of the EPD electrolyte solution for 30 min, EPD was performed by applying a constant DC voltage at −5.0 V vs. the Pt electrode for 60 s at room temperature. The obtained Ln₂CuO₄ modified/Al₂O₃ electrodes were washed with ethanol, and dried at 100°C, then finally sintered at 600°C for 1 h. The crystal structures of the obtained powders were elucidated by X-ray diffraction (XRD) analysis using Cu Kα₁ radiation (λ = 0.15405 nm) (XRD, Ultima IV, Rigaku Ltd.). Chemical states of metals and oxide on the surface of the oxide powders were characterized by X-ray photoelectron spectroscopy (XPS) (AXIS Nova, Shimadzu Kratos Ltd.) using an Al Kα source, in which the all binding energies were calibrated by an Au₄f line of 83.8 eV. Cyclic voltammetry (CV; scanning rate at 10 mV/s), differential pulse voltammetry (DPV) and amperometric measurements were performed by an electrochemical analyzer (model 1140A, ALS Ltd.) using a Pt plate and an Ag/AgCl (KCl sat.) as the counter and reference electrodes, respectively. The DPV measurement was performed by fixing the pulse width (0.05 s), pulse amplitude (50 mV), the pulse period (0.5 s) with the potential increment being 4 mV from the rest potential to +1.0 V vs. Ag/AgCl. All electrochemical experiments were carried out in 0.1 M, pH 7.0 Tris-HCl buffer solution of 60 mL at 30°C. Amperometric sensing properties were measurement by batch method in which reagent grade of NaNO₂ or other sodium salts (NaNO₃, Na₂SO₃, NaCl) solution was dropped step-by-step into the analytic solution using a micro pipet to control the ion concentrations.

Figure 1 shows the XRD patterns of Ln₂CuO₄ (Ln: Gd, Pr, Sm) powders after calcination at 800°C for 2 h by polymer precursor method. At calcination temperatures less than 750°C, impurity phases were detected in these oxides. Powders calcined at 800°C mostly contain single-phase layered perovskite-type oxide. However, specific surface areas of the obtained Ln₂CuO₄ (Ln: Gd, Pr, Sm) powders were as small as 1.53, 1.44, and 1.10 m²/g, respectively.

Figure 2(a) shows cyclic voltammograms of the Ln₂CuO₄ (Ln: Gd, Pr, Sm) electrodes in 1.0 × 10⁻³ M NaNO₂ aqueous solution. The CVs in the Ln₂CuO₄ (Ln: Gd, Pr, Sm) based electrodes showed increase in anodic and cathodic currents. Cathodic reactions are easy to be considered as the hydrogen evolution, and anodic currents should involve an electrochemical oxidation reaction including NO₂⁻, which is dependent on the catalytic activity of the oxides and the CVs should include in the NO₂⁻ and NO₃⁻ electrochemical redox reaction. Figure 2(b) shows cyclic voltammograms of the Gd₂CuO₄ electrode in various concentration of NaNO₂. It can be seen that the anodic current depended on the NO₂⁻ concentration. Interestingly, the Gd₂CuO₄ based electrode showed redox peaks at approximately ±0.20 V vs. Ag/AgCl, which was related to the redox properties of Cu in the oxide. In order to eliminate the back ground currents, the DPV of the Ln₂CuO₄ (Ln: Gd, Pr, Sm) based electrodes was investigated and the results are shown in Fig. 2(c). The DPVs of these electrodes showed clear increase in anodic currents at +0.80 V vs. Ag/AgCl, as shown in Fig. 2(c). In addition, Gd₂CuO₄ based electrode showed another peak at around +0.2 V which shall be attributed to Cu redox, as seen in the CV and the DPV as shown in Figs. 2(b) and 2(d), respectively.

As the large anodic currents were observed at +0.80 V, anodic current responses to NO₂⁻ of the Ln₂CuO₄ (Ln: Gd, Pr, Sm) electrodes at +0.85 V vs. Ag/AgCl were measured. Even though the steady state responses to NO₂⁻ ion were not observed for the Ln₂CuO₄ (Ln: Pr, Sm), the Gd₂CuO₄ based electrode gave quick and good response characteristics to NO₂⁻ ion as shown in Fig. 3. Interestingly, the amperometric response was not obtained in the solution after N₂ was bubbled, so the response shall be attributed to the presence of dissolved oxygen. The Gd₂CuO₄ based electrode showed a linear sensitivity between 8.0 × 10⁻⁴ and 5.0 × 10⁻³ M with very high sensitivity of 130 mA M⁻¹ cm⁻², as shown in Fig. 4. The 90% response time from 3.0 to 5.0 mM was about 1 min. Anion selectivity of the Gd₂CuO₄ based electrode was further investigated. No significant amperometric response at +0.85 V vs. Ag/AgCl was observed for NO₃⁻, SO₄²⁻, and Cl⁻ anions at a range between 10 μM and 5 mM, as shown in Fig. 5. Thus, the Gd₂CuO₄ based electrode exhibited high selectivity to NO₂⁻.

In order to investigate the sensing mechanism, surface chemical analyses were investigated for these oxide powders after calcination in air. XPS spectra at O₁s and Cu₂p of Ln₂CuO₄ (Ln: Gd, Pr, Sm) powders were shown in Fig. 6.
In O1s, lower and higher binding energy (BE) peaks were identified as lattice oxide (OL) and OA, respectively.\(^{28}\) It was seen that BE for OL in the Gd\(_2\)CuO\(_4\) powder shifted to higher value among the Ln\(_2\)CuO\(_4\) (Ln: Gd, Pr, Sm) powders. Although the OA peak in the Gd\(_2\)CuO\(_4\) powder was almost the same BE value among the Ln\(_2\)CuO\(_4\) (Ln: Gd, Pr, Sm) powders, an adsorbed hydroxide ion (OH\(^-\)) peak was additionally observed for the Gd\(_2\)CuO\(_4\). It should be considered that the chemically OA species on the Gd\(_2\)CuO\(_4\) was easily to react with water to give adsorbed hydroxide ions among the Ln\(_2\)CuO\(_4\) (Ln: Gd, Pr, Sm) powders. As for the Cu2p, all cuprates contains Cu\(^{+}\), especially Sm\(_2\)CuO\(_4\) and Gd\(_2\)CuO\(_4\) had large amount of Cu\(^{+}\) than Cu\(^{2+}\) at their surfaces.

Fig. 2. Cyclic voltammograms (a, b) and differential pulse voltammograms (c, d) of the Ln\(_2\)CuO\(_4\) (Ln: Gd, Pr, Sm) based electrodes in 0.1 M Tris-HCl buffer solution at 30°C.

Fig. 3. Response transient of the Gd\(_2\)CuO\(_4\) based electrode to NO\(_2^-\) at +0.85 V vs. Ag/AgCl.

Fig. 4. Dependence of response current on NO\(_2^-\) concentration of the Gd\(_2\)CuO\(_4\) based electrode at +0.85 V vs. Ag/AgCl.

Fig. 5. Dependence of response current on (a) NO\(_2^-\), (b) NO\(_3^-\), (c) Cl\(^-\) and (d) SO\(_3^{2-}\) concentration of the Gd\(_2\)CuO\(_4\) based electrode at +0.85 V vs. Ag/AgCl.

In O\(_{1s}\), lower and higher binding energy (BE) peaks were identified as lattice oxide (O\(_{l}\)) and O\(_{a}\), respectively.\(^{28}\) It was seen that BE for O\(_{l}\) in the Gd\(_2\)CuO\(_4\) powder shifted to higher value among the Ln\(_2\)CuO\(_4\) (Ln: Gd, Pr, Sm) powders. Although the O\(_{a}\) peak in the Gd\(_2\)CuO\(_4\) powder was almost the same BE value among the Ln\(_2\)CuO\(_4\) (Ln: Gd, Pr, Sm) powders, an adsorbed hydroxide ion (OH\(^-\)) peak was additionally observed for the Gd\(_2\)CuO\(_4\). It should be considered that the chemically O\(_{a}\) species on the Gd\(_2\)CuO\(_4\) was easily to react with water to give adsorbed hydroxide ions among the Ln\(_2\)CuO\(_4\) (Ln: Gd, Pr, Sm) powders. As for the Cu\(_{2p}\) all cuprates contains Cu\(^+\), especially Sm\(_2\)CuO\(_4\) and Gd\(_2\)CuO\(_4\) had large amount of Cu\(^+\) than Cu\(^{2+}\) at their surfaces.
From these results, the following sensing mechanism is tentatively proposed.

\[
\text{Gd}_2\text{CuO}_4 \rightleftharpoons \text{Oad}^2^- \quad \text{(in air)} \quad + \quad \text{H}_2\text{O} \\
\rightarrow \text{Gd}_2\text{CuO}_4 \rightleftharpoons 2\text{OHad}^- \quad \text{(in solution)} \\
\text{Cu}^+ \quad \text{(in Gd}_2\text{CuO}_4) \rightleftharpoons 2\text{OHad}^- \quad + \quad \text{NO}_2^- \\
\rightarrow \text{Cu}^{2+} \quad \text{(in Gd}_2\text{CuO}_4) \quad + \quad \text{NO}_3^- \quad + \quad 3\text{e}^- \quad + \quad \text{H}_2\text{O} \quad \text{(2)}
\]

At first, oxygen was adsorbed on the oxide in air. It then reacted with H\textsubscript{2}O in the solution to produce OH\textsuperscript{-}, as shown in reaction (1). Then, the oxidation reaction of NO\textsubscript{2}\textsuperscript{-} with adsorbed OH\textsubscript{ad} is predicted to have occurred at the Cu\textsuperscript{+} site of Gd\textsubscript{2}CuO\textsubscript{4}, as shown in reaction (2). Therefore in this manner it is proposed that Cu\textsuperscript{+} and adsorbed hydroxide ions (OH\textsuperscript{-}) play vital roles in NO\textsubscript{2}\textsuperscript{-} sensing.

However, the sensing mechanisms of the present electrochemical device using Gd\textsubscript{2}CuO\textsubscript{4} still need further quantitative investigation.

In conclusions, Ln\textsubscript{2}CuO\textsubscript{4} (Ln: Gd, Pr, Sm) powders were prepared by polymer precursor method, and their oxide thick-film electrodes were prepared by EPD method. Among the Ln\textsubscript{2}CuO\textsubscript{4} (Ln: Gd, Pr, Sm) based electrodes, Gd\textsubscript{2}CuO\textsubscript{4} based electrode showed very high sensitivity to NO\textsubscript{2}\textsuperscript{-} at 130 mA M\textsuperscript{-1} cm\textsuperscript{-2} between 8.0 × 10\textsuperscript{-4} and 5.0 × 10\textsuperscript{-3} M with high selectivity and fast response time. The high NO\textsubscript{2}\textsuperscript{-} sensitivity of Gd\textsubscript{2}CuO\textsubscript{4} is suggested to be derived from the electrochemical reaction from existing Cu\textsuperscript{+} within Gd\textsubscript{2}CuO\textsubscript{4} and adsorbed OH\textsuperscript{-}.

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