Amperometric Nitrite-Ion Sensor Based on Electrodeposited Sm-Based Perovskite-Type Oxide Thick-Film Electrode

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Perovskite-type oxide SmBO$_3$ ($B = \text{Cr, Mn, Fe, Co}$) powders were prepared by a polymer precursor method at 750 °C and systematically investigated for electrochemical sensing properties for NO$_2^\text{−}$. The SmBO$_3$-modified carbon-felt electrodes could be prepared by an electrophoretic deposition (EPD) method without sintering. Among the oxide deposited electrodes, the SmFeO$_3$ modified electrode showed the highest sensitivity to NO$_2^\text{−}$ with $11.9 \text{ mA M}^{-1} \text{ cm}^{-2}$ and a linear sensing range between $5.0 \times 10^{-5}$ and $1.0 \times 10^{-3}$ M at $+0.85 \text{ V vs Ag/AgCl}$ with high selectivity for NO$_2^\text{−}$ and no response to most other anions. A good correlation was observed between electrochemical activity toward nitrite-ion oxidation and oxygen adsorption properties of the oxides.

1. Introduction

It is known that nitrite ion (NO$_2^\text{−}$) reacts easily with proteins to produce carcinogenic N-nitrosamines which cause esophageal cancer and methemoglobinemia in vivo. Although it is used as an antioxidant for foods and beverages, nitrite ion itself is highly toxic, and it should be at a concentration less than 65 μM in drinking water according to the standards of the World Health Organization (WHO). It is also well known that NO$_2^\text{−}$ causes eutrophication in closed water systems. Thus, quantitative analysis of NO$_2^\text{−}$ has become very important. Thus far, nitrite ion is typically analyzed by a spectrophotometric method$^{(1,2)}$ or by ion chromatography, but these methods are complicated and not suitable for on-site monitoring. In contrast, electrochemical methods have aroused considerable interest as possibilities for the design of compact and low-cost ion sensors. As electrochemical NO$_2^\text{−}$ sensing materials, various metal complexes$^{(3,4)}$ as ionophores for potentiometric sensors, and carbon nanomaterials$^{(5,6)}$ metal nanomaterials$^{(7-12)}$ metal organic complexes$^{(13,14)}$ and conducting polymers$^{(15)}$ for amperometric sensors have been reported. Oxide-based NO$_2^\text{−}$ sensing materials, such as hollow Fe$_2$O$_3$ nano-polyhedrons$^{(16)}$, Fe$_2$O$_3$ nanoparticle-decorated reduced graphene oxide nanosheets$^{(17)}$, and nanoporous Fe$_2$O$_3$-CoO composites$^{(18)}$ have been developed. These sensors revealed a remarkable interaction between elemental iron and NO$_2^\text{−}$. These results indicated that iron-based mixed oxides might be suitable candidate materials

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for NO$_2^-$ sensing. We have proposed various electrochemical ion sensors for the hydrogen phosphate ion$^{(19)}$ and hydrogen peroxide$^{(20)}$ based on the considerable electrocatalytic properties of perovskite-type oxides. It has also been reported that Sm-based perovskite-type oxides showed high sensing abilities among the lanthanoids (La, Nd, Sm, Gd, and Dy)$^{(21,22)}$. In this study, we have systematically evaluated electrochemical catalytic activities of perovskite-type oxide Sm$_3$BO$_3$ ($B =$ Cr, Mn, Fe, Co)-modified carbon-felt electrodes prepared by electrophoretic deposition (EPD) for amperometric NO$_2^-$ sensing. The SmFeO$_3$ modified carbon-felt electrode showed the highest NO$_2^-$ sensing properties; these properties were related to the amount and the strength of adsorbed oxygen on the surface of the SmFeO$_3$.

2. Experimental

2.1 Preparation of perovskite-type oxide powders

Perovskite-type oxide Sm$_3$BO$_3$ powders were prepared by a polymer precursor method.$^{(23,24)}$ A 10 mmol quantity of metal (Sm, Cr, Mn, Fe, Co) nitrate of reagent grade was dissolved in 50 mL of ethylene glycol (EG), which was mixed with 40 mmol of acetylacetone (AcAc) as a coordinating agent and 7.5 wt% polyethylene glycol (PEG: MW 200) as a polymer additive, until a viscous sol was formed. These polymer precursor solutions were dried in ambient air to form xerogel powders, which were then heat-treated at 750 °C for 2 h. The crystal structures of the powders obtained were elucidated by X-ray diffraction (XRD) analysis using CuKα radiation ($λ = 0.15405$ nm) (X-ray diffraction spectroscopy, Ultima IV, Rigaku Ltd.). The specific surface area (SSA) of the powders was determined by Brunauer, Emmett, and Teller (BET) method from nitrogen adsorption isotherms obtained at 77 K using an automatic specific surface area analyzer (BELSORP-mini-II, MicrotracBEL 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 binding energies were calibrated using the C$_1s$ line at 284.6 eV. Temperature programmed desorption (TPD) experiments were carried out using a catalyst analyzer (BELCAT-B-SPS, MicrotracBEL Ltd.) as follows. Each sample was evacuated for 15 min at 750 °C, then exposed to 50 mL/min of oxygen for 1 min at the same temperature, and cooled to 50 °C in the same atmosphere. After the evacuation, the sample was heated at a rate of 10 °C/min in a helium stream (30 mL/min), and desorbed oxygen was monitored by a thermal conducting detector.

2.2 Preparation of perovskite-type oxide thick films by EPD

SmBO$_3$ modified carbon-felt (SmBO$_3$/CF) electrodes were prepared by EPD.$^{(25)}$ A 0.24 g sample of each oxide powder was suspended in 50 mL AcAc and mixed in a planetary ball mill (L-P1, Ito Seisakusho Co., Ltd.) at 250 rpm for 30 min. After the ball-mill treatment, 25 mg I$_2$ and 50 mL AcAc were added to make an EPD electrolyte solution. EPD was carried out using carbon felt (CF; GF-20-2F, Nippon carbon Ltd.) as a working electrode and a Pt plate as a counter electrode. The distance between the 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 −50 V vs the Pt electrode for 10 min at room temperature. The SmBO$_3$/CF electrodes were washed with ethanol and dried at 100 °C. Further sintering of the electrodes was not carried out.
2.3 Electrochemical measurements

Cyclic voltammetry and amperometric measurements were performed using an electrochemical analyzer (model 1140A, ALS Ltd.) using a Pt plate and an Ag/AgCl (KCl sat.) as the counter and a reference electrodes, respectively. Figure 1 shows a diagram of the sensor electrode using oxide modified carbon felt. All electrochemical experiments were carried out in 50 mL pH 7.0 Tris-HCl buffer solution at 30 °C after oxygen or nitrogen bubbling for 30 min. Amperometric sensing properties were measured by a batch method using solutions of reagent grade NaNO2 or other sodium salts (NaNO3, Na2SO4, Na2HPO4, NaHCO3, CH3COONa, and NaSCN) added dropwise to the analyte solution with a micropipette to control the ion concentrations.

3. Results and Discussion

3.1 Characterization of the oxide powders

Figure 2 shows the XRD patterns of SmBO3 (B = Cr, Mn, Fe, Co) powders prepared at 750 °C for 2 h by the polymer precursor method. The powders consisted of primarily single-phase perovskite-type oxide. The SSAs of SmCrO3, SmMnO3, SmFeO3, and SmCoO3 were between 1.9 and 8.6 m² g⁻¹ as shown in Table 1. SEM images of these powders are shown in Fig. 3. SmCrO3 and SmCoO3 powders were partially sintered and formed large particles as shown by their smaller SSAs. Although SmMnO3 powder consisted of small particles less than 50 nm in diameter, these particles aggregated partially to form larger particles. Among them, SmFeO3 powder consisted of relatively small particles of ca. 90 nm in diameter.
3.2 Electrochemical measurements

Figure 4 shows cyclic voltammograms of the SmBO\textsubscript{3}/CF (B = Cr, Mn, Fe, Co) electrodes in aqueous solutions at various NO\textsub{-}\textsubscript{2} concentrations with oxygen bubbling. The cyclic voltammograms in SmCrO\textsubscript{3}, SmMnO\textsubscript{3}, and SmCoO\textsubscript{3} systems showed an increase in anodic current depending on NO\textsub{-}\textsubscript{2} concentration; however, they still had large hysteresis even in a buffer solution. The hysteresis in SmCrO\textsubscript{3}, SmMnO\textsubscript{3}, and SmCoO\textsubscript{3} systems should be primarily due to the redox of transition metals (Cr, Mn, Co) in the perovskite-type oxides. However, the anodic current of the SmFeO\textsubscript{3}/CF electrode around +0.85 V vs Ag/AgCl increased simply with increasing NO\textsub{-}\textsubscript{2} concentration.

Figure 5 shows a typical transient response curve of the SmFeO\textsubscript{3}/CF electrode to various concentration of NO\textsub{-}\textsubscript{2} at +0.85 V vs Ag/AgCl. The anodic current of the SmFeO\textsubscript{3}/CF electrode increased with increasing NO\textsub{-}\textsubscript{2} concentration. The 90% response time from 100 to 200 μM was about 3 min. The dependence of response current on NO\textsub{-}\textsubscript{2} concentration of the SmFeO\textsubscript{3}/CF electrode under O\textsubscript{2} and N\textsubscript{2} bubbling is shown in Fig. 6. Response currents increased with increasing NO\textsub{-}\textsubscript{2} concentration with O\textsubscript{2} and N\textsubscript{2} bubbling. The response current under O\textsubscript{2} bubbling was slightly larger than that with N\textsubscript{2}, especially in the lower concentration range. The SmFeO\textsubscript{3}/CF electrode

Table 1

| BET S.A. (m\textsuperscript{2} g\textsuperscript{-1}) | SmCrO\textsubscript{3} | SmMnO\textsubscript{3} | SmFeO\textsubscript{3} | SmCoO\textsubscript{3} | Fe\textsubscript{2}O\textsubscript{3} |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Sensitivity (mA M\textsuperscript{-1} cm\textsuperscript{-2}) | 9.9 | 4.3 | 11.9 | 9.4 | 4.5 |
| Linear range (μM) | 200–1000 | 200–900 | 50–1000 | 100–800 | 100–1000 |
| \(\frac{O_A}{(O_A + O_L)}\) (%)* | 43.5 | 36.8 | 46.3 | 44.0 | 14.7 |

*at +0.85 V vs Ag/AgCl.

**\(O_A\): amount of adsorbed oxygen, \(O_L\): amount of lattice oxygen.

Fig. 3. SEM images of SmBO\textsubscript{3} (B = Cr, Mn, Fe, Co) powders.
showed a linear sensitivity between $5.0 \times 10^{-3}$ and $6.0 \times 10^{-3}$ M with a sensitivity of 11.9 mA M$^{-1}$ cm$^{-2}$ under O$_2$ bubbling. This may be related to the reaction with the adsorbed oxygen as described in the following. Hereafter, all response characteristics were measured with O$_2$ bubbling. Figure 7 shows response characteristics of the SmBO$_3$/CF ($B = \text{Cr, Mn, Fe, Co}$) and Fe$_2$O$_3$/CF electrodes. The NO$_2^-$ sensitivity for the SmBO$_3$/CF systems was in the order SmFeO$_3 >$ SmCrO$_3 >$ SmCoO$_3 >$ SmMnO$_3 =$ Fe$_2$O$_3$, as summarized in Table 1. This means that the SmFeO$_3$ perovskite-type structure plays an important role in electrochemical oxidation of NO$_2^-$ ion. These results also indicated that the Fe surface in the oxides might be the active site for the reaction with NO$_2^-$; Fe in SmFeO$_3$ has higher surface activity for NO$_2^-$ than Fe in Fe$_2$O$_3$. 

Fig. 4. Cyclic voltammograms of SmBO$_3$/CF electrodes for various NO$_2^-$ concentrations (Scan rate: 10 mV/s).

Fig. 5. Response transient curve of the SmFeO$_3$/CF electrode to NO$_2^-$ (+0.85 V vs Ag/AgCl).

Fig. 6. Dependence of response current on NO$_2^-$ concentration of the SmFeO$_3$/CF electrode with O$_2$ or N$_2$ bubbling (+0.85 V vs Ag/AgCl).
The SmFeO$_3$/CF electrode showed no significant amperometric response at +0.85 V vs Ag/AgCl for NO$_3^-$, SO$_4^{2-}$, HPO$_4^{2-}$, CH$_3$COO$^-$, HCO$_3^-$, and SCN$^-$ anions between 10 and 1000 μM. Thus, the SmFeO$_3$/CF electrode exhibited high selectivity for NO$_2^-$.

3.3 Sensing mechanism

To investigate the sensing mechanism, surface chemical analysis was carried out by XPS and TPD. First, XPS spectra at O$_1s$ of SmBO$_3$ (B = Cr, Mn, Fe, Co) powders were recorded as shown in Fig. 8. Lower and higher binding energy (BE) peaks were identified as lattice oxide (O$_{L}$) and adsorbed oxygen (O$_{A}$), respectively. The O$_{A}$ / (O$_{A}$ + O$_{L}$) ratio on the surface of SmFeO$_3$ was the highest among the SmBO$_3$ systems as shown in Table 1. Figure 9 compares XPS spectra between Fe$_2$O$_3$ and SmFeO$_3$ at O$_{1s}$ and Fe$_{2p}$. The amount of adsorbed oxygen on Fe$_2$O$_3$ was very small compared with that on SmFeO$_3$. The BE of lattice oxygen in Fe$_2$O$_3$ was relatively large as shown in Fig. 9 (a); thus, Fe$_2$O$_3$ crystals are characterized by strong metal-oxygen bonding. Oxidation states of Fe in Fe$_2$O$_3$ and SmFeO$_3$, included Fe$^{2+}$, Fe$^{3+}$, and Fe$^{4+}$ as shown in Fig. 9(b). The presence of Fe$^{2+}$, especially in SmFeO$_3$, should allow the high valence of Fe$^{4+}$ and/or oxygen vacancies in the oxide.

To investigate the oxygen adsorption-desorption properties of perovskite-type oxides, TPD profiles of the SmBO$_3$ (B = Cr, Mn, Fe, Co) powders were determined. As shown in Fig. 10, two peaks appear at around 250 °C and over 450 °C in the TPD profiles of the SmBO$_3$ (B = Cr, Mn, Fe, Co) powders. The former and latter peaks seem to be chemically bonded surface oxygen and lattice oxygen, respectively. Oxygen desorption of chemically bonded surface oxygen from the SmFeO$_3$ was noted from ca. 240 °C, which was the lowest observed temperature for the SmBO$_3$ (B = Cr, Mn, Fe, Co) series. From these TPD and XPS measurements, the surface of the SmFeO$_3$ has the most active oxygen species among the oxides.
From these results, the sensing mechanism may be expressed as Eqs. (1) and (2):

\[
\text{SmFeO}_3\text{O}_{\text{ad}}^{-} + \text{H}_2\text{O} \rightarrow \text{SmFeO}_3\text{O}_{\text{ad}}^{-}2\text{OH}_{\text{ad}}^{-} \tag{1}
\]

\[
\text{SmFeO}_3\text{O}_{\text{ad}}^{-}2\text{OH}_{\text{ad}}^{-} + \text{SmFeO}_3\text{NO}_2^{-} \rightarrow \text{SmFeO}_3 + \text{NO}_3^{-} + 2e^{-} + \text{H}_2\text{O} \tag{2}
\]

A possible reaction responsible for \(\text{NO}_2^{-}\) response was proposed to be the oxidation reaction of \(\text{NO}_2^{-}\) by adsorbed \(\text{OH}_{\text{ad}}^{-}\) on a Fe site in \(\text{SmFeO}_3\). The electrocatalytic activity for \(\text{NO}_2^{-}\) oxidation
is thought to be influenced by the presence of OH\textsuperscript{−}\textsubscript{ad} on the oxide surface which was formed by the reaction between O\textsubscript{ad} and H\textsubscript{2}O. In these results, the SmFeO\textsubscript{3}/CF electrode showed higher sensitivity than the Fe\textsubscript{2}O\textsubscript{3}/CF or other electrodes.

4. Conclusions

The Sm\textsubscript{B}O\textsubscript{3} (B = Cr, Mn, Fe, Co) powders could be prepared by a polymer precursor method at 750 °C. The Sm\textsubscript{B}O\textsubscript{3}-modified CF electrodes were fabricated by an EPD method without sintering. Among the oxides tested, the SmFeO\textsubscript{3}/CF electrode showed the highest NO\textsubscript{2} sensitivity, 11.9 mA M\textsuperscript{−1} cm\textsuperscript{−2}, and a wide linear response range between 5.0 × 10\textsuperscript{−5} and 1.0 × 10\textsuperscript{−3} M. Furthermore, the SmFeO\textsubscript{3}/carbon electrode showed no response to NO\textsubscript{3}, SO\textsubscript{4}\textsuperscript{2−}, HPO\textsubscript{4}\textsuperscript{2−}, CH\textsubscript{3}COO\textsuperscript{−}, HCO\textsubscript{3}−, and SCN\textsuperscript{−} up to 1000 μM. The high NO\textsubscript{2} sensitivity of SmFeO\textsubscript{3} arises from the large amount of adsorbed oxygen, which should strongly correlate to the electrocatalytic activity of NO\textsubscript{2} oxidation.

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