Solid Electrolyte Gas Sensor Based on a Proton-Conducting Graphene Oxide Membrane

Azumi Miyamoto,† Yuta Kuwaki,‡ Toshifumi Sano,† Kazuto Hatakeyama,† Armand Quitain,‡ Mitsu Sasaki,§ and Tetsuya Kida*†‡

†Department of Applied Chemistry and Biochemistry, Faculty of Engineering, ‡Division of Materials Science, Faculty of Advanced Science and Technology, and §Institute of Pulsed Power Science, Kumamoto University, Kumamoto 860-8555, Japan

Supporting Information

ABSTRACT: Graphene oxide (GO) is an ultrathin carbon nanosheet with various oxygen-containing functional groups. The utilization of GO has attracted tremendous attention in a number of areas, such as electronics, optics, optoelectronics, catalysis, and bioengineering. Here, we report the development of GO-based solid electrolyte gas sensors that can continuously detect combustible gases at low concentrations. GO membranes were fabricated by filtration using a colloidal solution containing GO nanosheets synthesized by a modified Hummers’ method. The GO membrane exposed to humid air showed good proton-conducting properties at room temperature, as confirmed by hydrogen concentration cell measurements and complex impedance analyses. Gas sensor devices were fabricated using the GO membrane fitted with a Pt/C sensing electrode. The gas-sensing properties were examined by potentiometric and amperometric techniques. The GO sensor showed high, stable, and reproducible responses to hydrogen at parts per million concentrations in humid air at room temperature. The sensing mechanism is explained in terms of the mixed-potential theory. Our results suggest the promising capability of GO for the electrochemical detection of combustible gases.

INTRODUCTION

Solid electrolyte gas sensors have been widely used for emission control, process control, and environmental protection in various fields.1,2 Carbon monoxide (CO) sensors composed of proton conductors, such as perfluoro-3,6-dioxo-4-methyl-7-octenesulfonic acid (Nafion; Du Pont), are an important example of such sensors.3–5 These devices are also called fuel-cell-type sensors and utilize a change in the electrode potential or electrical current upon interaction with gas to produce the sensor signal. In particular, fuel-cell-type CO sensors have gained a large market share, particularly in the United States and Europe, due to their good performance and low power consumption.

The prototype of this sensor was developed by Miura et al.,6 who reported that a proton-conducting Nafion membrane fitted with noble metal electrodes showed good electromotive force (EMF) responses to combustible gases, such as H2 and CO, in air at room temperature. The EMF response did not follow Nernstian behavior, indicating the simultaneous occurrence of anodic and cathodic reactions that generate a mixed potential at the sensing electrode. Zirconium phosphate and antimonial acid were also used as proton conductors in this sensor.7,8 Furthermore, they applied this sensor to the amperometric detection of H2 and CO. The electrical currents generated from electrochemical reactions of the target gases are linearly dependent on the gas concentration.9 The good sensing performance at room temperature makes this device suitable for practical and commercial applications. Several types of polymeric proton conductors have been developed.10,11 However, very few materials have been applied in this type of gas sensor.12–14 A probable reason for this is that Nafion has several advantages over other materials, including high proton conductivities (approximately 10−3 S cm−1) at room temperature, excellent thermal and mechanical stability, and flexibility.

In this study, we applied graphene oxide (GO) as a new material in solid electrolyte gas sensors. GO is a two-dimensional carbon nanosheet covered with oxygen-containing functional groups and can be synthesized via the oxidation and exfoliation of graphite. GO serves as a precursor of graphene. However, its versatile functionalities, which are different from those of graphene, have recently attracted much attention for use in various applications, including catalysis, batteries, capacitors, solar cells, etc.15–17 In particular, due to the proton-conducting properties of GO,18–20 GO membranes have successfully been applied to fuel cells.21–23 Thus, it is readily expected that GO is a potential material for fuel-cell-
type gas sensors. GO has already been applied to several gas sensors, such as resistive sensors,\textsuperscript{24} impedance sensors,\textsuperscript{25} transistor sensors,\textsuperscript{26} and optical sensors.\textsuperscript{27,28} However, to the best of our knowledge, the application of GO to solid electrolyte gas sensors has not yet been reported. The advantages of GO are that it is composed of earth-abundant carbon and does not contain rare or toxic elements, the fabrication of GO membranes is not complex, and no expensive or large facilities are required for its production. This is in distinct contrast to the high price of Na\textsubscript{2}SO\textsubscript{4}Na\textsubscript{2}SO\textsubscript{4} resulting from its complicated and very toxic production routes.\textsuperscript{29,30} Furthermore, a GO membrane is an assembly of nanosheets and, as such, the membrane can accommodate water in its interlayer. Thus, GO sensors may function even at low relative humidity (RH). Here, we demonstrate the potential capability of GO-based solid electrolyte gas sensors. The proton-conducting properties of GO membranes were studied by hydrogen concentration cell measurements and complex impedance analyses. Using GO membranes, sensor devices were fabricated and their gas-sensing properties to combustible gases was examined by potentiometric and amperometric methods. The sensing mechanism was also discussed in terms of the electrode reaction kinetics.

### EXPERIMENTAL SECTION

**Synthesis of GO Colloids.** GO nanosheets were synthesized from graphite powder via a modified Hummers’ method.\textsuperscript{31} First, graphite powder (2.0 g) was added to concentrated sulfuric acid (92 mL) under stirring, followed by the addition of sodium nitrate (2.0 g). The mixture was cooled in an ice bath for 30 min. Subsequently, potassium permanganate (10 g) was added slowly into the mixture. Then, the reaction system was slowly transferred to a water bath and heated at 35 °C for 40 min. Distilled water (92 mL) was added slowly to the solution, which was stirred for another 5 h in an oil bath at 95 °C. Additionally, distilled water (200 mL) and hydrogen peroxide were added until the color of the solution changed from brown to yellow. After cooling, the product was recovered by centrifugation at 3000 rpm for 5 min. The recovered precipitate was washed with an aqueous HCl solution (5%) three times to remove metal ions. The removal of acid was achieved by repeated washing with distilled water and subsequent centrifugation. The obtained solid was dispersed in distilled water, followed by ultrasonication for 4–6 h. The resulting dispersion was subjected to centrifugation at 10 000 rpm for 30 min to remove aggregates. Finally, the supernatant was separated to obtain a colloidal suspension containing GO nanosheets.

**Fabrication of the GO Membrane.** A self-supporting membrane was fabricated on two filter membranes stacked together using the GO suspension (3.5 mg/mL) by vacuum filtration. One filter membrane had 0.4 μm pores, whereas the other had 180 μm pores. The 180 μm filter was used as the supporting filter for the 0.4 μm filter. The filtration process produced a GO membrane with a thickness of 180 μm. This process was carried out under atmospheric air conditions.

**Materials Characterization.** The synthesized GO nanosheets were analyzed by X-ray diffraction (XRD) using Cu Kα radiation (MiniFlex600; Rigaku). The presence of oxygen-containing functional groups on GO was analyzed by Fourier transform infrared (FT-IR) spectroscopy (FTIR4100; JASCO) and X-ray photoemission spectroscopy (XPS, PHI 1600; PerkinElmer). GO membranes synthesized by the above method were used for the XRD, FT-IR, and XPS analyses. The morphology of the GO membrane was analyzed by scanning electron microscopy (SEM, JSM-7600F; JEOL). The proton conductivity of the GO membrane was examined by complex impedance spectroscopy. Pt electrodes were sputtered onto both sides of the membrane, and the electrical contacts were composed of Ni meshes and Ni wires. The impedance was measured in air under humid conditions (2–90% RH) at room temperature by an impedance analyzer (1260; Solartron).

**Sensor Fabrication and Sensing Tests.** Two types of sensors were fabricated. Figure 1a shows the structural schematic of the concentration cell-type GO sensor. The device was fitted with commercial Pt (46.3%)/C (TEC10E50E; Tanaka Holdings Co., Ltd.) as the sensing electrode. A Pt/C powder was dispersed in isopropanol, and the suspension was dropped onto the GO membrane to form the sensing layer. Pt-black was coated on the other side of the membrane as the reference electrode. A Ni mesh was used as the current collector. Two types of sensors were fabricated.
reference electrode. To fix the potential of the reference electrode, atmospheric air was introduced to the reference electrode side. The electrodes were covered with Ni meshes (50 mesh). This device structure was also used for hydrogen concentration cell measurements, in which hydrogen in Ar was introduced to the sensing and reference electrodes. In this case, Pt/C was used for both the sensing and reference electrodes. The structure of a planar-type sensor is shown in Figure 1b. Pt/C was used as the sensing electrode, whereas a Perovskite-type oxide was used as the counter electrode. Perovskite-type oxide La0.6Sr0.4Co0.78Ni0.02Fe0.2O3 was prepared by an evaporation method.32 The perovskite-type oxide powder was mixed with distilled water to form a paste, which was applied to one side of the GO membrane and dried at room temperature. The sensing and counter electrodes were exposed to the sample gases.

The sample gases, including hydrogen, oxygen, and ethanol, were prepared by mixing parent commercial gases with synthetic air and were introduced to the sensing electrode side. Water vapor was prepared by bubbling synthetic air through distilled water and mixed with the dry sample gases to control the RH. The RH of the sample gas was determined by a humidity sensor. The flow rate of the sample and reference gases was 100 mL/min. The EMF generated between the sensing and counter electrodes was measured with an electrometer. The sensor response was defined as $|\Delta EMF|$ (EMF in gas − EMF in air). For the amperometric detection of hydrogen, the planar-type gas sensor was used. The electrical currents ($I$) generated with the applied voltage (1.2 V) were measured with an electrometer. The sensor response was defined as $|\Delta I|$ ($I$ in gas − $I$ in air). All measurements were carried out at room temperature.

RESULTS AND DISCUSSION

Characterization of GO. Figure 2a shows a representative FT-IR spectrum of GO. The peaks corresponding to the vibrational modes of oxygen-containing functional groups are clearly observed in the spectrum. Namely, the presence of hydroxyl (O−H, C−OH), carboxyl and carbonyl (C=O), and epoxy (C−O−C) groups can be confirmed.33,34 Figure 2b shows the C (1s) XPS spectrum of GO. The peak at 285 eV corresponds to C−C, C=O, and C−H bonds, whereas the peak at 287 eV can be attributed to the C−OH, C−O−C, and C=O bonds. The small peak at 289 eV is attributed to the O−C=OH bonds in the carboxyl groups. The peak assignments were made according to the literature.33,35 The deconvoluted XPS spectrum suggests a high content of epoxy groups in GO. The oxygen content in GO was determined to be 57 wt %.

Figure 2c shows the particle size distribution of a colloidal GO suspension. The particle size ranged from 70 to 800 nm. The size distribution is rather wide, suggesting the partial decomposition of GO nanosheets during the oxidation process. The GO suspension showed excellent colloidal stability; no particle sedimentation occurred when the suspension was stored for over a year. The surface charge of the GO nanosheets was determined to be −80 mV by zeta potential measurements. This highly charged surface should originate from the presence of oxygen-containing functional groups at the surface, which prevented the aggregation of GO nanosheets in the suspension. Figure 2d shows the XRD pattern of a membrane composed of GO nanosheets. The GO membrane exhibited a peak at a low angle of 10.78°, which is typical for layered materials. The interlayer distance of the stacked GO nanosheets was determined to be 8.20 Å, which is in good agreement with the reported results.33−35 The stacking of GO nanosheets can also be confirmed by the cross-sectional SEM image of the GO membrane, as shown in Figure S1 (Supporting Information).
The obtained membrane was pinhole-free and dense, as confirmed by He permeation tests. Potentiometric Response of the Concentration Cell-Type GO Sensor. To examine proton conduction in the GO membrane, the EMF response of a hydrogen concentration cell containing the GO membrane was measured. The concentration of hydrogen in Ar (90% RH) was changed from 1 to 5%, whereas the concentration was fixed to 5% at the reference side. Figure 3 shows the EMF response of the concentration cell upon changing the hydrogen concentration at room temperature. The EMF was linearly dependent on the logarithm of the hydrogen concentration, obeying the Nernst equation as follows

\[
\text{EMF} = \frac{RT}{nF} \ln \frac{C_{H_2}^\circ}{C_{H_2}},
\]

where \( R \) is the gas constant, \( T \) is the absolute temperature, \( F \) is the Faraday constant, \( n \) is the reaction number, \( t \) is the transport number, and \( C_{H_2} \) is the hydrogen concentration. The slope of the curve was calculated to be 28.75 mV/decade, which is close to the theoretical value of 29.53 mV/decade if it is assumed that \( t \) equals unity. In this case, the following equilibrium reaction is assumed to proceed at the electrodes

\[
2H^+ + 2e^- \rightleftharpoons H_2
\]

Thus, the results clearly indicate that proton conduction occurs in the GO membrane and protons are in electrochemical equilibrium with hydrogen in the gas phase. The proton conduction should result from the presence of oxygen-containing functional groups, as confirmed by the FT-IR and XPS results (Figure 2). However, a deviation from the theoretical value was observed in the slope, suggesting the occurrence of electron conduction in GO. Taking this into consideration, \( t \) can be calculated to be 0.91. A \( t \) value lower than unity has also been reported for a GO membrane by Gao et al.\textsuperscript{23} They reported that treatment with ozone increased the proton conductivity of GO due to an increase in the content of oxygen-containing functional groups. Thus, the low \( t \) value may result from the removal of oxygen-containing functional groups from GO during measurements in which the GO membrane was exposed to highly reducing conditions. On the other hand, we reported previously that the controlled removal of oxygen-containing functional groups makes GO a mixed (proton and electron) conducting material.\textsuperscript{36,37} Nevertheless, the results confirmed that the GO membrane fitted with Pt/C electrodes strongly responded to changes in the hydrogen concentration at room temperature, although electron conduction also occurred in the GO membrane.

We next applied the GO membrane for the detection of hydrogen in parts per million (ppm) concentration in air. The in situ sensing of hydrogen is very important for the detection of hydrogen leakage during its production, storage, and utilization. Figure 4 shows the EMF response of the GO sensor in air (35% RH) containing hydrogen (50–300 ppm) at room temperature as a function of hydrogen concentration. Atmospheric air was introduced to the reference electrode in this case. The GO sensor quickly responded to hydrogen. Its EMF was very stable and reproducible, as shown in Figure S2. The EMF repeatedly stabilized upon repeated cycles of exposure to \( H_2 \) and air atmospheres. The 90% response and recovery times were below 10 and 15 min, respectively. The sensor response, defined as \( \Delta \text{EMF} \), was dependent on the hydrogen concentration and was linearly related to the logarithm of the hydrogen concentration, as observed for the concentration cell. The observed good hydrogen-sensing ability should result from proton conduction in the GO membrane, which occurs along the oxygen-containing functional groups. It should be noted that the slope of the curve (86 mV/decade) was 3 times larger than that for the concentration cell (28.75 mV/decade). Such deviation from the ideal behavior expected from the Nernst equation was first observed in zirconia-based oxygen sensors.\textsuperscript{38,39} The generation of the large EMF response is explained by the mixed-potential theory.\textsuperscript{40} According to this theory, the simultaneous occurrence of the following anodic and cathodic reactions can be suggested in the present case

\[
H_2 \rightarrow 2H^+ + 2e^-
\]

\[
\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O
\]

Miura et al. proposed the following equation to show the dependence of EMF on the gas concentration by considering that the net current is zero when the two reactions occur simultaneously:\textsuperscript{40}

\[
E_m = E_0 - m_1 \ln C_{H_2} + m_2 \ln C_{O_2}
\]
where $E_m$ is the mixed potential and $m_A$ and $m_B$ are constants. This equation is valid provided that oxygen reduction and hydrogen oxidation both obey the Butler−Volmer equation or oxygen reduction follows the Butler−Volmer equation and hydrogen oxidation is limited by mass transport. The observed EMF response was in good agreement with the EMF behavior expected from the above equation; the EMF was dependent on the logarithm of the hydrogen concentration, and the slope of the curve, corresponding to $m_A$, had a negative value ($-86 \text{ mV/decade}$). Thus, the results indicate that the EMF response of the GO sensor is explained by the mixed-potential theory. This means that the response is kinetically controlled by the two electrochemical reactions.

Principally, this type of sensor responds to combustible gases such as CO and alcohol. Here, we examined the sensitivity to ethanol to examine the selectivity for hydrogen, as shown in Figure 5a. The sensor response to ethanol was negligibly small. The small response to ethanol is probably due to the efficient heterogeneous combustion of ethanol at the Pt/C electrode because a relatively thick sensing electrode (ca. 100 mm) was used. This limits the diffusion of ethanol to the three-phase interface (TPI) between GO and Pt/C, significantly decreasing the sensor response to ethanol. In contrast, the diffusion rate of hydrogen is probably high even in such a thick film electrode. Control of the microstructure and thickness of the sensing electrode would lead to sensor responses to various gases, such as ethanol and toluene, as reported for high-temperature mixed-potential-type gas sensors. The response to oxygen was also examined in the absence of hydrogen. The GO sensor responded to oxygen, as shown in Figure 5a. The response trend was similar to that of the hydrogen concentration cell (Figure 3). The dependence of EMF on the oxygen concentration was linearly related to the logarithm of the oxygen concentration, and the slope was 13 mV/decade, which is in good agreement with the theoretical slope (14.8 mV/decade) for the oxygen equilibrium reaction with $n = 4$ shown below.

$$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$$ (6)

Thus, in the absence of combustible gases, the response to oxygen obeys Nernstian behavior. It can be concluded that the GO sensor is not sensitive to small changes in the oxygen concentration because the observed and theoretical EMF dependence on the oxygen concentration is small. Figure 5b shows the effects of RH on the EMF response to hydrogen. The EMF values to hydrogen and their dependence on the hydrogen concentration (slope of the curve) were influenced by a change in humidity, but the influence was not significant at 20−50% RH. On the other hand, no stable response was obtained under dry conditions, as shown in Figure S3.

To elucidate the cause of the humidity effect on the EMF response, the proton conductivity and charge-transfer resistance at different relative humidities were analyzed by complex impedance spectroscopy. Figure 6a shows the complex impedance plane plots (Cole−Cole plots) of the GO membrane in air with different relative humidities at room temperature. The plots are well-fit to the equivalent circuit shown in the inset of Figure 6a. Fitting with the equivalent

![Figure 5](https://example.com/figure5.png)

**Figure 5.** (a) EMF responses to ethanol and oxygen in air (35% RH) at room temperature for the concentration cell-type sensor with an air reference. (b) Effect of humidity on the response to hydrogen (10−50% RH).

![Figure 6](https://example.com/figure6.png)

**Figure 6.** (a) Cole−Cole plots of the complex impedance of the GO membrane in air at different relative humidities. (b) Proton conductivity and charge-transfer resistance ($R_{ct}$) as a function of RH.
circuit yields the bulk resistance \( (R_b) \) and charge-transfer resistance \( (R_{ct}) \) at different relative humidities, as shown in Table 1. The proton conductivity (through-plane) was calculated using \( R_b \), the electrode area, and the membrane thickness. Figure 6b shows the proton conductivity and \( R_{ct} \) as a function of RH. The proton conductivity gradually increased with increasing RH, reaching \( 16 \times 10^{-3} \) S cm\(^{-1} \) at 80% RH. Notably, the proton conductivity was not lost when the GO membrane was under dry conditions and showed almost constant values at 2–60% RH. The GO membrane is an assembly of thin graphene nanosheets, and the sheets are hydrophilic due to the presence of oxygen-containing functional groups. Thus, water can be stably accommodated in the interlayer, avoiding a drastic decrease in the proton conductivity. The results confirm the good proton conductivity of the GO membrane even at low humidity. In contrast, \( R_{ct} \) largely increased at low humidity. Such drastic increase in \( R_{ct} \) likely impedes the electrochemical reaction at the TPI. Indeed, the response was unstable under dry conditions, as shown above (Figure S3). Thus, the results suggest that electrochemical reactions at the TPI are suppressed in dry air, leading to unstable EMF response. On the other hand, the influence of humidity on the response was not significant at 20–50% RH, as shown in Figure 5b. The good proton conductivity and low \( R_{ct} \) at 20–60 RH% may reduce the interference of humidity.

However, unstable EMF responses were observed at 700–800 ppm H\(_2\), as shown in Figure S4. The response gradually decreased at higher hydrogen concentrations. It is suggested that water accumulates as condensation from the gas phase and by hydrogen combustion, blocking the TPI and decreasing the response to hydrogen. Indeed, at lower H\(_2\) concentrations, stable responses were observed. Such an adverse effect can be overcome by controlling the microstructure of the electrode. Decreasing the thickness or increasing the porosity of the electrode would avoid the accumulation of byproducts at the TPI and produce stable responses.

### Table 1. Proton Conductivity (Through-Plane) and Charge-Transfer Resistance \( (R_{ct}) \) at Different Relative Humidities

| RH (%) | \( R_b \) (Ω) | Proton Conductivity (S cm\(^{-1} \)) \( \times 10^{-3} \) | \( R_{ct} \) (Ω) \( \times 10^3 \) |
|-------|---------|---------------------|-----------------|
| 2     | 63      | 2.01                | 360             |
| 35    | 45      | 2.08                | 4.10            |
| 50    | 35      | 2.11                | 1.13            |
| 60    | 30      | 2.46                | 0.82            |
| 70    | 20      | 5.71                | 0.65            |
| 80    | 5       | 16.14               | 0.38            |

The sensor response (\( \Delta \text{EMF} \)) was linearly related to the logarithm of the hydrogen concentration. We confirmed that the perovskite-type oxide is not sensitive to hydrogen at room temperature using a concentration cell-type sensor with the air reference electrode, as shown in Figure S5. The use of materials inert to hydrogen for the counter electrode allows us to measure a change in the sensing electrode potential using a planar-type device. The observed stable response indicates that the potential at the counter electrodes is fixed even when the hydrogen concentration was changed. Thus, no efficient anodic oxidation of hydrogen was thought to have occurred at the perovskite-type oxide/GO interface due to its low catalytic activity at room temperature, fixing the counter electrode potential almost constant. On the other hand, the perovskite-type oxide has good oxygen reduction activity,\(^4\) and as such, the oxygen reaction (eq 6) can reach equilibrium to achieve stable EMF responses.

The above results indicate that the potentiometric detection of hydrogen is possible with the planar-type sensor. However, accurate concentration determination is sometimes difficult due to the semilogarithmic dependence of EMF on the gas concentration. In contrast, for amperometric detection, a linear dependence of the sensor signal on the concentration can be obtained. Thus, we attempted to detect hydrogen by measuring the electrical currents generated upon electrochemical reactions driven by applied voltage. Figure 8 shows the change in the response of the planar GO sensor with a perovskite-type oxide counter electrode and the dependence of the electrical currents on hydrogen concentration. The electrical currents were generated as a result of the anodic and cathodic reactions.

### Potentiometric and Amperometric Responses of the Planar-Type GO Sensor

As shown above, our concentration cell-type sensor works well as a hydrogen sensor. However, this structure is not practical and difficult to downsize. To demonstrate the practical feasibility of the GO sensor, a planar-type sensor was fabricated and tested for its sensor response to hydrogen. Figure 7 shows the EMF response to hydrogen of the planar-type GO sensor fitted with a perovskite-type oxide (La\(_{0.6}\)Sr\(_{0.4}\)Co\(_{0.78}\)Ni\(_{0.22}\)Fe\(_{0.2}\)O\(_3\)) as the counter electrode at room temperature. The cobalt-based perovskite-type oxide is known to show a high electrochemical oxygen reduction activity.\(^4\) In addition, with this material, the operating temperature of a solid electrolyte oxygen sensor can successfully be lowered.\(^4\) The sensor quickly responded to a change in the hydrogen concentration, and the dependence of the sensor response (\( \Delta \text{EMF} \)) was linearly related to the logarithm of the hydrogen concentration. We confirmed that the perovskite-type oxide is not sensitive to hydrogen at room temperature using a concentration cell-type sensor with the air reference electrode, as shown in Figure S5. The use of materials inert to hydrogen for the counter electrode allows us to measure a change in the sensing electrode potential using a planar-type device. The observed stable response indicates that the potential at the counter electrodes is fixed even when the hydrogen concentration was changed. Thus, no efficient anodic oxidation of hydrogen was thought to have occurred at the perovskite-type oxide/GO interface due to its low catalytic activity at room temperature, fixing the counter electrode potential almost constant. On the other hand, the perovskite-type oxide has good oxygen reduction activity,\(^4\) and as such, the oxygen reaction (eq 6) can reach equilibrium to achieve stable EMF responses.

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The obtained sensor response (ΔI) was linearly related to the hydrogen concentration, as expected. Currently, more detailed assessments of the amperometric sensing properties, such as the cross-sensitivity and stability, are in progress.

This study clearly shows that both potentiometric and amperometric detection of hydrogen is possible with the planar GO sensor. One important property of the GO membrane is its water-storing capability, which allows protons to diffuse in the interlayer. This property can be controlled by tuning the size of the GO nanosheets, the amount of oxygen-containing functional groups, and the thickness of the membrane. For gas detection, the reactivity of combustible gases, such as hydrogen and CO, on the GO membrane is important. Tuning the catalytic activity of the electrode improves aspects of the sensor performance such as the sensitivity, selectivity, and stability. Further development of the GO-based sensor is also feasible based on its excellent prospective characteristics as a sensor material. The structure and composition of GO can be facilely controlled by several routes, including the hybridization of GO with noble metals, metal oxides, and molecular catalysts; surface functionalization with organic compounds; and the doping of foreign elements into the GO framework. Modification by such methods would drastically change the catalytic and electrochemical properties of the GO membrane, thereby improving the sensitivity, selectivity, and stability of the GO sensor. Because GO itself is a single-layer nanosheet, ultramiinaturization of the electrochemical GO sensor is also possible, as was reported for ultrasmall graphene-based transistor-type gas sensors.

■ CONCLUSIONS

A colloidal suspension of GO nanosheets was synthesized by a modified Hummers’ method starting from graphite powder. Filtration using the colloidal suspension produced a self-standing GO membrane (180 μm) free of pinholes. Proton conduction in the GO membrane was confirmed by hydrogen concentration cell measurements. Sensor devices were fabricated by attaching Pt/C and Pt-black to the GO membrane as sensing and reference electrodes, respectively. The sensor using atmospheric air as a reference gas showed good EMF responses to hydrogen (50–300 ppm) in air (35% RH) at room temperature. The EMF was linearly related to the logarithm of the hydrogen concentration. The slope of the curve was 3 times higher than that expected from the Nernst equation, indicating that the generation of EMF upon the introduction of hydrogen is explained in terms of the mixed-potential theory. The sensor response was influenced by humidity, and no stable response was observed under dry conditions. Complex impedance analyses suggest that electrochemical reactions at the TPI are impeded in the absence of water, causing the EMF response to be unstable. A planar-type sensor was also fabricated using solid reference electrodes composed of a perovskite-type oxide that is not sensitive to hydrogen. The planar GO sensor also showed good EMF responses to hydrogen in air at room temperature. Amperometric detection of hydrogen was also possible using the planar-type sensor.

■ ASSOCIATED CONTENT

* Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00239.

Photograph and cross-sectional SEM image of a GO membrane, cyclic response of the sensor, response transients in dry air, response transients to hydrogen with higher concentrations, and response transients of the GO sensor with sensing electrodes made of perovskite-type oxide (PDF)

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: tetsuya@kumamoto-u.ac.jp. Fax: +81-96-342-3679.

ORCID
Armand Quitain: 0000-0003-1051-3726
Tetsuya Kida: 0000-0001-9357-9557

Notes
The authors declare no competing financial interest.

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