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# Planar-type $BiCuVO_x$ solid electrolyte sensor for the detection of volatile organic compounds☆

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ABSTRACT

Mixed potential-type gas sensors with a $BiCuVO_x$ ($Bi_2Cu_{0.1}V_{0.9}O_{5.35}$) oxygen conductor, fitted with composite electrodes made of perovskite-type oxide ($La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$) and $BiCuVO_x$, were tested for their organic gas sensing properties. A planar-type $BiCuVO_x$-based device, in which thin sensing electrode and thick counter electrode are attached, exhibited good sensing characteristics to low ethanol concentrations (4–30 ppm) at 400 °C. The electromotive force (EMF) of the device had a linear relation to the logarithm of ethanol concentration. The 90% response and recovery times of the device were short, i.e., less than 1 min. Moreover, the planar structure successfully eliminated any oxygen interference. The ethanol sensing mechanism is based on the mixed potential generation from the simultaneous anodic oxidation of ethanol and the cathodic reduction of oxygen, at the $BiCuVO_x$/electrode interface.


## 1. Introduction

Solid electrolyte-based potentiometric gas sensors are widely used for the detection of various air pollutant gases, including $CO_2$ [1–4], $NO_x$ [5–11], $SO_x$ [12–15], $Cl_2$ [16,17], CO [18–20], hydrocarbons [21–26], $NH_3$ [27–29], and $H_2S$ [30–32]. In particular, mixed-potential-type gas sensors have recently attracted much attention because of their superior properties such as sensitivity, response speed, and structural simplicity. The earliest version of these sensors was reported about 30 years ago [18]. For these gas sensors, the type of solid electrolyte used is quite important; the use of solid electrolytes with high ionic conductivities at low temperatures, such as antimony oxide [27,33,34] and Nafion [32], allows the detection of CO and $H_2$ at room temperature. On the other hand, sensors using solid electrolytes that operate at high temperatures, such as stabilized zirconia [8,9,11,15,17–20,22,24,29,30] and doped ceria [23,25], allows the detection of $NO_x$, CO, and hydrocarbons in high temperature exhausts. Particularly for high temperature sensors, the sensor response and selectivity are significantly dependent on the type of the electrode material used. It has been reported that oxide electrodes such as $SnO_2$ [20,24], $WO_3$ [11], CdO [20,24], $ZnFe_2O_4$ [9], and $LaMnO_3$ [25] show high sensitivity to the above gases. These results show the importance in selecting the appropriate materials for creating highly selective gas sensors.

Recently, we have reported that a mixed-potential-type $BiCuVO_x$ ($Bi_2Cu_{0.1}V_{0.9}O_{5.35}$; oxygen ion conductor)-based device, fitted with perovskite-type oxide ($La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$; mixed electro- and ionic-conductor) electrodes, can detect organic gas molecules such as formaldehyde and ethanol at a lower temperature range (350–400 °C) [35]. The successful operation at lower temperatures likely stems from the high oxide ion conductivity of $BiCuVO_x$ [36,37] and the high electro-catalytic activity of the perovskite-oxide [38]. We have also confirmed that the composite electrode of $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$ and $BiCuVO_x$ has good stability against humidity and $CO_2$ [39]. These observations directly demonstrate the features which make the sensor practical for application.

However, the fabricated device is still a prototype structure, i.e., concentration cell-type structure (two-chamber cell) supplied with a reference gas (air). For practical application, the device structure needs to be redesigned. In a planar structure, the electrodes are exposed to the target gas atmosphere; this compact structure can be readily applied in the field. Metal electrodes with high electrochemical activity to oxygen, such as Pt, are frequently used as counter (reference) electrodes for planar zirconia-based sensors fitted with oxide sensing electrodes [40–45]. However, Pt cannot be used as a counter (reference) electrode in $BiCuVO_x$-based sensors because Pt does not sufficiently promote the electrochemical reaction of oxygen at low temperatures such as 350 °C, as reported previously

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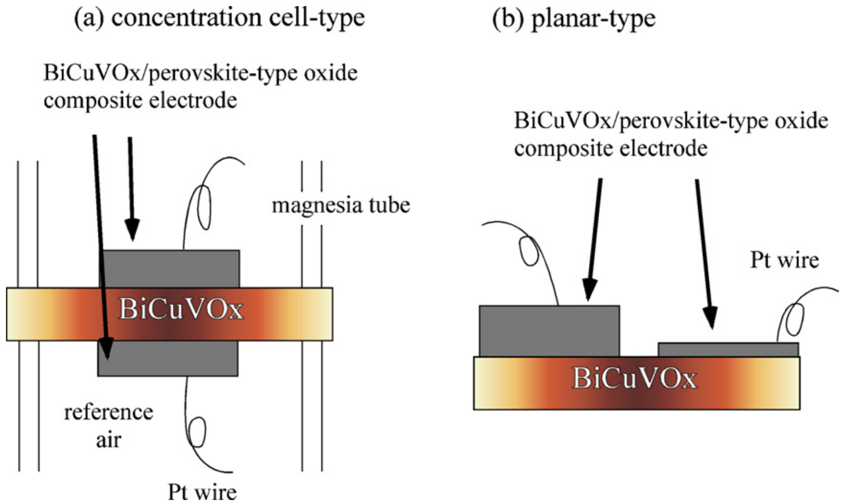


**Fig. 1.** Schematic of the device structure. (a) Concentration cell-type (two-chamber cell) and (b) planar-type devices.

[46]. Another approach uses various thicknesses of perovskite-type oxide electrodes for the sensing and counter (reference) electrodes of $BiCuVO_x$-based sensors. We expected that increasing the thickness of the oxide counter electrode would reduce the number of organic gas molecules that reach the counter electrode/solid electrolyte interface. This would degrade or decrease the counter electrode response to organic gases.

In this study, a planar-type device was fabricated and tested for its gas sensing properties. This design attempts to optimize the structure of a $BiCuVO_x$ sensor fitted with perovskite-type oxide electrodes. To control the gas sensitivity of the planar-type device, two perovskite-type oxide electrodes of different thicknesses were used as sensing and counter electrodes. We examined the sensitivity, selectivity, and response speed of the $BiCuVO_x$-based sensors. These basic gas sensing properties were evaluated to determine the sensors' suitability for applications.

## 2. Experimental

A $BiCuVO_x$ ($Bi_2Cu_{0.1}V_{0.9}O_{5.35}$) disk (10 mm in diameter and 1.0 mm in thickness) was prepared by a solid state reaction between $Bi_2O_3$, $V_2O_5$, and CuO precursors. The $BiCuVO_x$ disk obtained was dense, gas tight and free of pinhole defects. A perovskite-type oxide ($La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$) was prepared by an amorphous malic precursor method. The detailed preparation procedures of $BiCuVO_x$ and $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$ were reported elsewhere [46]. Fig. 1 shows the structures of the fabricated sensor devices. Two types of devices were fabricated: (a) concentration

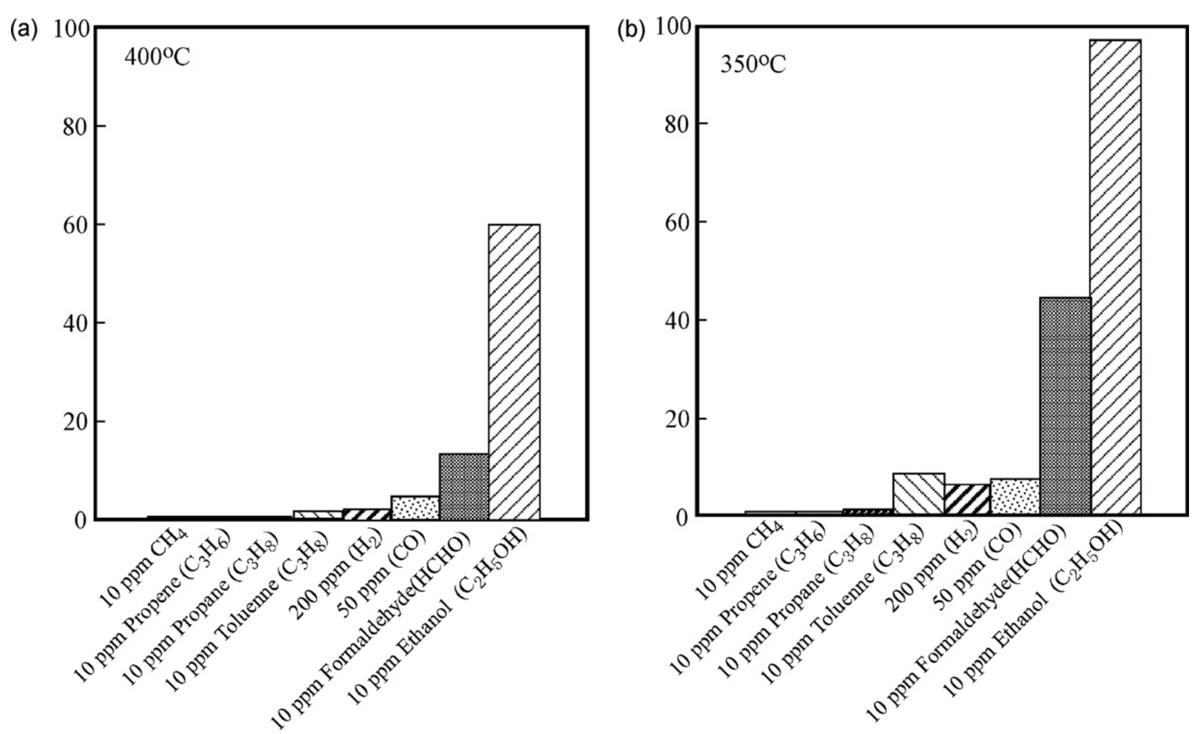


**Fig. 2.** Sensitivities of the concentration cell-type device to methane (10 ppm), propene (10 ppm), propane (10 ppm), CO (50 ppm), $H_2$ (200 ppm), toluene (10 ppm), formaldehyde (10 ppm), and ethanol (10 ppm) at (a) 400 °C and (b) 350 °C.