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Electrochemical property of proton-conductive manganese dioxide for sensoring hydrogen gas concentration

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ABSTRACT

A high-purity, ramsdellite-crystal type manganese dioxide (Koyanaka et al., 2005 [1]; Iikubo et al., 2010 [2]) was used for an electrolyte in a hydrogen gas sensor (Ueda et al., 2011 [3]). In this report, the electrochemical properties of the hydrogen gas sensor using electrolytes made of different crystal types of manganese dioxides, such as the ramsdellite-crystal type, a β-crystal type, and a λ-crystal type were examined. The high-purity, ramsdellite-crystal type manganese dioxide showed the conductivity from 7.1×10^{-5} S/cm (80 °C) to 1.7×10^{-4} S/cm (25 °C) under 85% relative humidity condition. This conductivity was probably based on the proton conduction on the MnO_2 particles.

1. Introduction

Hydrogen gas (H_2) promises to be a major clean fuel in the near future. Thus, sensors that can measure the concentration of hydrogen gas over a wide dynamic range are in demand for the production, storage, and utilization of hydrogen gas. However, it is difficult to measure hydrogen gas concentrations greater than 10% using conventional sensors directly [4–14]. In our previous study, a simple sensor using an electrolyte made of a high-purity, ramsdellite-crystal type manganese dioxide (RMO) that enabled in-situ measurements of hydrogen gas concentration over a wide range of 0.1–99.9% at room temperature, was reported [3]. Manganese dioxide (MnO_2) crystallizes into various phases [15]. This variation in crystal structure gives rise to a variety of intriguing physical and chemical functions. MnO_2 crystal structure is based on edge- and corner-sharing of the basic structural units of MnO_6 octahedra and various types of crystal structure such as α, β, γ, R, ε, δ, and λ are formed by this array of the unit (See Supplementary data Fig. 6).

In this study, the sensor capability to various concentrations of H_2 and the conductivity was examined using electrolytes made of different crystal types MnO_2, such as the RMO (orthorhombic structure [16]), β-MnO_2 (rutile structure [17]), and λ-MnO_2 (spinel structure [18]). This study aimed to examine electrochemical properties such as Arrhenius plots and Nyquist plots regarding electrolytes made of different crystal structures of MnO_2. The difference of crystal structure had influenced significantly the H_2 sensoring ability in the sensor system [3].

2. Material and methods

RMO was prepared according to a previously reported method [1]. And the method to make a pellet of the MnO_2 electrolyte was described in the other previous report [3]. λ-MnO_2 and the β-MnO_2 were prepared according to the methods of Refs. [19,20], respectively. The output voltage from the H_2 sensor was measured using a voltmeter which has a high internal resistance of 10 MΩ. The temperature dependence of the conductivity and the impedance for each MnO_2 electrolyte were examined by using alternating current (AC) impedance methods.

3. Experimental

Fig. 1 shows a schematic of the sensor system, where the platinum (Pt) meshwork pieces (100 mesh sizes, 2 cm diameter) attached to each side of the pellet served as the electrodes and also as catalysts for the $H_2 \rightarrow 2\,H^+ + 2e^-$ dissociation. We determined voltages generated between the Pt electrodes as a function of the H_2 concentration

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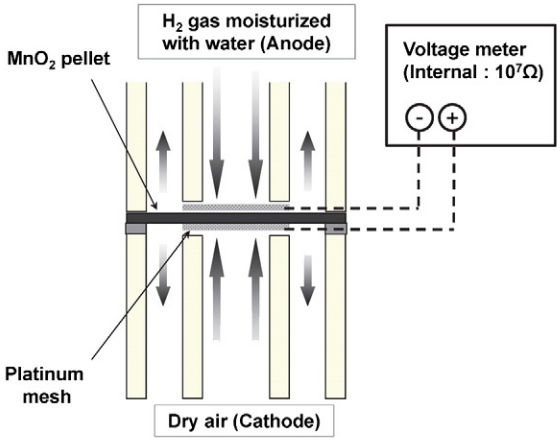

Fig. 1. Schematic of the hydrogen gas (H_2) sensor unit. The H_2 was supplied to the upper surface (anode) of the wet MnO_2 pellet (2 cm diameter, 0.6 mm thickness), while dry air was supplied to the opposite surface (cathode) in a housing unit made of perfluoroalkoxyalkane. The output voltage between the Pt electrodes (100 mesh size, 2 cm diameter) was measured for various H_2 concentrations from 1 to 99.9% balanced with argon gas (Ar). The internal resistance of the voltage meter was 10 MΩ. The H_2 and dry air flow rates were maintained at 100 or 20 mL/min. The output voltage was defined as the average voltage generated while supplying H_2 into the anode for 1 min. The response was defined as the average of the maximum values of dV/dt. Residual voltages were measured after purging H_2 from the anode with N_2 (99.9%) supplied for 1 min.

at room temperature. Distilled water (0.4 mL) was added onto the surface of each MnO_2 pellet (2 cm diameter, 0.6 mm thickness) before supplying H_2. H_2 was supplied to the upper surface (anode) of the wet MnO_2 pellet, while dry air was supplied to the opposite surface (cathode) in a housing unit made of perfluoroalkoxyalkane. The output voltage between the Pt electrodes was measured at various H_2 concentrations from 1% to 99.9%, where commercially-available mixed gases were used. The internal resistance of the multi meter (Agilent 34401A) was set to 10 MΩ. The temperature dependence of the conductivity was measured under 85% relative humidity (RH) condition without supplying H_2 on the anode, by a frequency response analysis of the AC impedance spectra. Solartron 1255B and SI 1287, AMETEK were employed. For the control of the experimental atmosphere (*i.e.* humidity–temperature), SH-240 ESPEC was used. Furthermore, the impedance of wet pellets was examined by using AC impedance method. The applied amplitude and AC frequency range were 100 mV and 10 mHz–1 MHz, respectively.

4. Results and discussion

Fig. 2(a) shows the output voltages between the Pt electrodes with the sequential supply of H_2 (1%–99.9%) and N_2 to the anode surface of the electrolyte pellet (N_2 was used to purge H_2 from the anode). Exposing the electrolyte to various concentrations of H_2 produced responses, within 0.5 s, in the output voltage, corresponding to the supply and purge of H_2. A saturation of output voltages was observed for H_2 concentrations greater than 10%. In a previous study [3], we reported that the response (*i.e.*, dV/dt) showed linearity, and the best-fit line of dV/dt was able to be used as the standard curve to calculate unknown concentrations of H_2 in a sample gas.

The sensor properties using electrolytes made of different MnO_2 crystal types were determined, and the results are compared in Fig. 2(b). (XRD patterns of tested MnO_2 are shown in the Supplementary data.) The RMO showed the highest response of 0.537 V/s and lowest residual voltage of 0.00199 V (*i.e.*, the voltage that remained after purging H_2 from the anode surface with N_2 supplied for 1 min). The β-type MnO_2 showed the lower output voltage and response compared to other types of MnO_2. And, the λ-type MnO_2 showed the highest output voltage of 0.980 V and the response of 0.479 V/s, but the residual voltage of 0.498 V was much higher than that of the RMO. This means that λ-type MnO_2 is not a good material for the electrolyte in this sensor for the sequential measurements of H_2 concentrations. As a result, the RMO showed the best properties for an H_2 sensor compared to the other crystal types of MnO_2 tested.

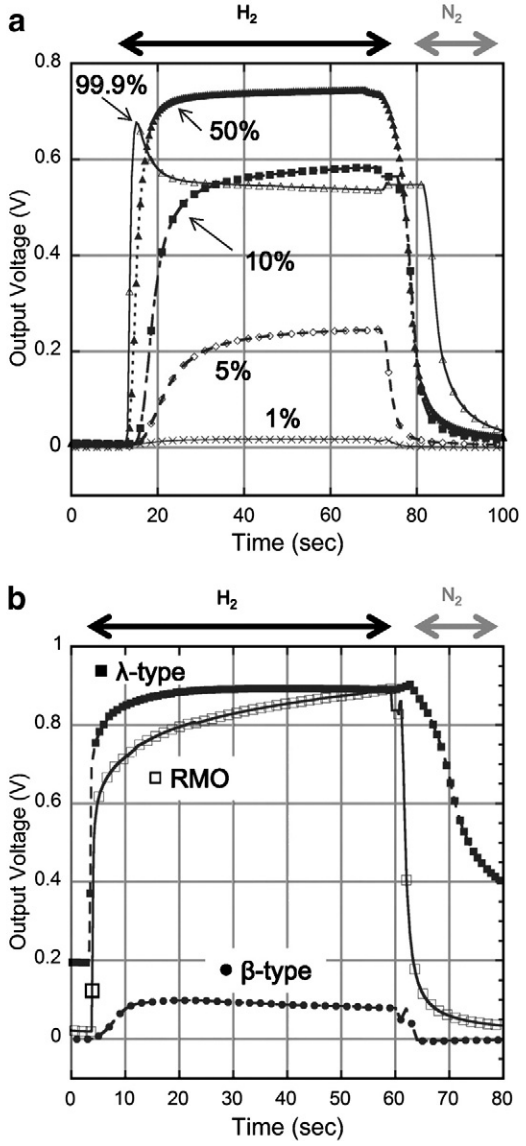

Fig. 2. Output voltages of the sensor system with various H_2 concentrations and electrolytes made of MnO_2 with different crystal structures (a) Comparison of H_2 sensing properties for various H_2 concentrations using electrolyte made of the R-type MnO_2. Dependence of the output voltage in various concentration of H_2 supplied to the system, using an H_2 flow rate of 20 mL/min to the anode surface of RMO electrolyte pellet. (b) Comparison of H_2 sensing properties for various electrolytes made of MnO_2 with different crystal structures. Dependence of the output voltage on electrolytes made of different crystal types MnO_2. H_2 (99.9%) was supplied for a flow rate of 100 mL/min to the anode surface of each electrolyte pellet. In both experiments of (a) and (b), N_2 (99.9%) was used for purging H_2 from the anode surface while dry air was supplied to the opposite surface (cathode).

Fig. 3 displays the temperature dependence of the conductivity (*i.e.* Arrhenius plots), which examined for electrolytes made of different crystal types MnO_2 under the wet condition of 85%RH. As a result, these crystal types MnO_2 showed clearly different conductivities. The RMO showed the conductivity from 7.1×10^{-5} S/cm at 80 °C to 1.7×10^{-4} S/cm at 25 °C. The activation energies (E) for each crystal type of MnO_2 were obtained as: $E_{\beta\text{-type}}=6.2\times10^{-2}$ kJ/mol, $E_{RMO}=13$ kJ/mol, and $E_{\lambda\text{-type}}=20$ kJ/mol. In addition, the β-type MnO_2 showed