Selective detection of hydrogen concentration in mixture gas with methane using an electrolyte made of manganese dioxide

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Introduction

Hydrogen (H_2) promises to be a major clean fuel in the near future. Thus, many kinds of H_2 sensors have been studying up to now. From the viewpoint of safe utilization, H_2 sensors that can operate around room temperature are preferable [1-4]. And H_2 is usually produced by a steam methane (CH_4) reforming reaction (i.e. $CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$) in industry. The production gas from the reforming reaction contains 2~10% concentrations of CH_4 as the residual. Thus, H_2 sensors that can measure a high concentration of H_2 in mixture gas that contained H_2 and CH_4 is in demand. However, it is difficult to directly measure H_2 concentrations greater than 10% using conventional H_2 sensor. Recently, a potentiometric type sensor using an electrolyte made of manganese dioxide that enabled in-situ measurements of H_2 concentration over a wide range of 0.1-99.9% at room temperature was reported [5,6]. The sensor can measure H_2 concentration by using the response, which was defined as the average of the maximum gradient of rising edges on output voltage curves $(dV/dt)_{max}$. In this study, we examined the selective sensing of H_2 concentration in mixture gas of H_2 and CH_4 for the H_2 sensor.

Experimental

The electrolyte of the MnO_2 pellet (0.8mm thickness, 2 cm diameter) was set as the anode in the H_2 sensor. Platinum (Pt) meshwork pieces (100mesh size, 2cm diameter) attached to each side of the wide pellet served as the electrodes and also as catalysts for the $H_2 \rightarrow 2H^+ + 2e^-$ dissociation. This sensor system is conceptually similar to that of a typical SOFC system. Mixed gas of H_2 and CH_4 was supplied to the anode surface of the wet MnO_2 electrolyte pellet (0.2mL/g water density), while the cathode surface exposed to atmosphere in the housing unit of the sensor. The flow of the mixture gas was maintained at 50mL/min. The output voltage generated between the Pt electrodes (i.e. the potential difference between the anode and the cathode) was measured for various H_2 concentrations such as 5, 10, and 20% in each mixture gas, which contained 10% of CH_4 constantly balanced with argon (Ar). The internal resistance of the voltage meter was 1M ohm.

Results and discussion

Fig. 1 shows the variation of the sensor response corresponding to H_2 concentrations in mixture gases of H_2 and CH_4. The responses $(dV/dt)_{max}$ were obtained as 344, 852, and 1779mV/sec corresponding to H_2 concentrations of 5, 10, and 20%, respectively. The response increased proportionally according to the increase of the H_2 concentration in sample gas. The result indicates that the CH_4 mixed in sample gas does not influence the measurement of the H_2 concentration on the sensor operation at room temperature. This capability for the selective detection of H_2 concentration is important for practical usages of the sensor. In addition, the sensor in this report does not need an additional system to supply dry air to the cathode compared to the previous system [5,6]. Thus, the sensor system became simple; however, the sensor response should be examined carefully compared with that of the previous system to understand the sensor properties. Currently, we expect on this sensor that the quantity of the necessary sample for measurements of H_2 concentration is much decreased (e.g. 1mL/min) compared to that of the previous system (e.g. 50mL/min).

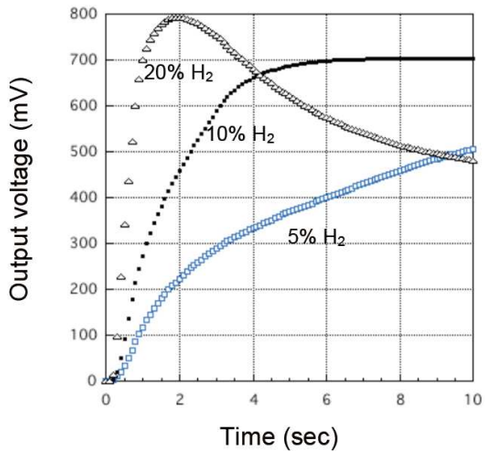

Fig. 1 Variation of the sensor response under a room temperature corresponding to H_2 concentrations in mixture gases which contained the H_2 (5, 10, and 20%) and the CH_4 (10%).

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