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Sensitive and Selective Detection of Hydrogen Using YSZ-based Sensor with Zn-Ta-based Oxide Sensing-electrode

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Abstract

An yttria-stabilized zirconia (YSZ)-based sensor utilizing a Zn-Ta-based oxide sensing electrode (SE) is reported herein as being capable of generating sensitive and selective response toward hydrogen (H_2). The addition of 84 wt.% Ta_2O_5 into ZnO brought about the highest response toward H_2, when compared with other examined Zn-Ta-based oxide SE materials. After a stabilization period of about 50 days, the sensor exhibited a stable and high sensitivity (Δemf) of approximately -600 mV toward 100 ppm H_2 and low cross-sensitivity towards other examined gases (< ± 80 mV) at 500°C under humid operating conditions (20 vol.% O_2 and 5 vol.% H_2O). An almost linear relationship between sensitivity and H_2 concentration (10-100 ppm) was observed for the developed sensor.

Keywords: Gas sensors, Hydrogen, YSZ, Potentiomentric, ZnO, Ta_2O_5

Introduction

Existing renewable energy such as wind or solar energy offerings are static systems which lack of portability, limiting potential applications; unlike H_2 which is compressible. H_2 has been touted as a potential substitute where petroleum is currently used, particularly when used with fuel cell driven vehicles and power generators. However, since H_2 is a colorless, odorless gas, with a low ignition energy (0.02 mJ), combined with a lower explosive limit of 4 vol.% has made it poses an explosive risk [1]. This has made the utilization of H_2 difficult as it poses a serious risk. Considering this, the demand for a device that can detect H_2 sensitively and selectively, is of great interest for safety monitoring applications. For high temperature applications, YSZ-based gas sensors have been acknowledged as one of the leading candidates for reliable and high-performance gas sensors during several decades, due to their good thermal and mechanical stability under harsh working conditions.

An attempt to utilize ZnO as a sensing electrode material for mixed-potential type YSZ-based sensors was investigated more than ten years ago [2]. However, the high response toward hydrogen was also accompanied by responses toward other examined gases. Two years later, it was reported that the addition of Ta_2O_5 into another metal oxide could yield selective catalytic properties [3]. Furthermore, the addition of Ta_2O_5 into SEs has been proven to improve the selectivity of a potentiometric sensor [4], and Ta_2O_5-based materials have been reported to give high sensitivity toward H_2 [5]. Hence, Ta_2O_5 was added into ZnO in this study and the sensing performances of the developed YSZ-based sensor using a Zn-Ta-based oxide SE were examined.

Experimental

The sensor was fabricated using a hemi-spherically terminated YSZ-tube (8 mol.% Y_2O_3-doped ZrO_2, Nikkato, Japan). Recently, our group has proposed the utilization of an intermediate layer of YSZ, in order to improve mechanical stability at the interface between SE and YSZ solid electrolyte. Therefore, an intermediate YSZ layer between the SE and the YSZ solid electrolyte was also fabricated here. In this process, YSZ powder (Tosoh Corp., Japan) was mixed with an organic binder (α-terpineol). The resulting paste was painted onto the surface of YSZ tube.

The sensing electrode material was fabricated by mixing commercial ZnO powder (Konjundo Chemical Lab., Japan) with Ta_2O_5 powder (Konjundo Chemical Lab., Japan) in a mortar. An organic binder (α-terpineol) was added into the mixed powder, making a uniform paste.

This paste was applied onto the surface of YSZ layer, which had been previously painted onto the YSZ tube, forming a 4 mm-wide band. The reference electrode (RE) was made by applying Pt paste (Tanaka, Kikinzoku, Japan) on the inner surface of the end of the YSZ tube. Subsequently, the assembled sensor was sintered at 1200oC for 2 h in air to form the SE and the RE.

The gas sensing characteristics of the fabricated sensors were evaluated at an operational temperature of 500°C under humid conditions (5 vol.% H2O). The potential difference between SE and Pt/air-RE was measured using a digital electrometer (R8240, Advantest, Japan), as a sensing signal. The crystal structure of the SE layers was analyzed with an X-ray diffractometer (XRD, RINT 2100VLR/PC, Rigaku, Japan) with Cu Kα radiation.

Results and Discussions

Figure 1 shows the preliminary test results for the sensor utilizing ZnO-SEs with different additions of Ta2O5. As shown in this figure, the sensor using ZnO(+84 wt.% Ta2O5)-SE showed the most sensitive response toward 400 ppm H2 (Δemf = -250 mV) when operated at 500oC under the humid conditions (5 vol.% O2 + 5 vol.% H2O), in comparison with other sensors using SEs with different percentage additions of Ta2O5, as well as the parental ZnO- and Ta2O5-SE. The sensor could generate not only a sensitive response toward H2, but also a relatively selective one, since the response toward other examined gases were also found to be low (e.g., Δemf towards CO = -45 mV, C3H8= -9 mV, C3H6 = -73 mV, NOx < ± 20 mV).

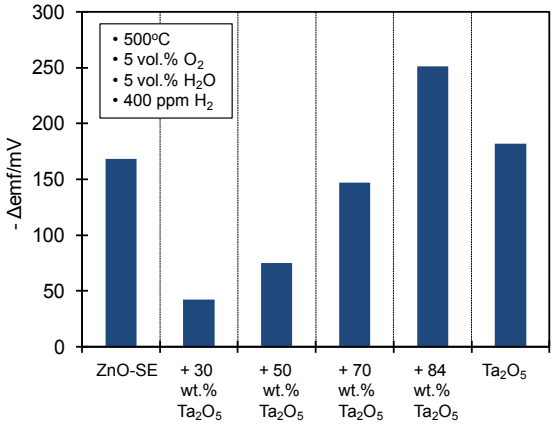

Fig. 1 The comparison of H2 response at 500oC of sensors utilizing ZnO with increasing addition and/or pure Ta2O5, as SE.

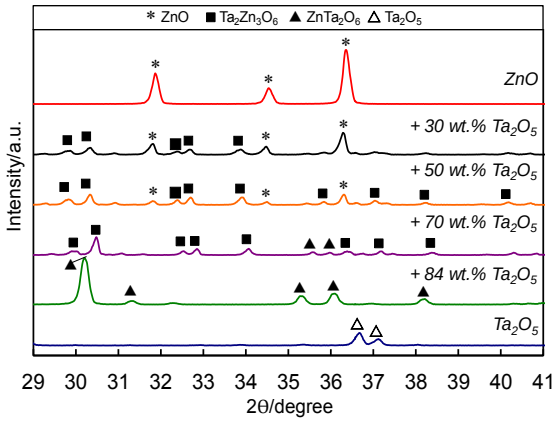

Fig. 2 The XRD patterns of ZnO-SE with different additions of Ta2O5 after sintering at 1200oC for 2 h.

The XRD pattern comparison of ZnO with different additions of Ta2O5 and pure Ta2O5 is presented in Fig. 2. It is seen that the addition of Ta2O5 to ZnO with increasing ratio resulted in a mixture of crystal phases and stoichiometries. The addition of 30 wt.% Ta2O5 was confirmed to form a mixture that was identified as being in good agreement with ZnO (JCPDS no.: 36-1451) and Ta3Zn2O6 (JCPDS no.20-1237). The XRD peaks for the ZnO(+ 50 wt.% Ta2O5) sample confirmed the formation of the similar mixture to the previous sample. This would explain the similar H2 response that both SEs generated. When the addition of Ta2O5 into ZnO was raised to 70 wt.%, the observed peaks were found to be in good agreement with a mixture of ZnTa2O6 (JCPDS no.: 39-1484) and Ta3Zn2O6, despite the occurrence of some minor peak shifting. However, when 84 wt.%

Ta_2O_5 was added into the ZnO, the resulting compound was identified as being single phase and in good agreement with $ZnTa_2O_6$.

Tab. 1: The cross sensitivity of the sensor utilizing ZnO(+ 84 wt.% Ta2O5)-SE toward different gases at 500oC under humid conditions (20 vol.% O2 + 5 vol.% H2O).

Gas (100 ppm)	Sensitivity (Δemf / mV)
H_2	-598
CO	-11
CH_4	-13
C_3H_8	-9
C_3H_6	-3
NO	-17
NO_2	25
NH_3	-38

The developed sensor was then maintained at 500°C to assess the long-term stability. After a stabilization period of 50 days, the sensor response (emf) toward H_2 was found to increase largely from –250 mV to –830 mV. Furthermore, the response stabilized at around -830 mV after the 50th day. This increase in H_2 sensitivity is believed to be due to both of the decreased catalytic activity to the cathodic reaction of O_2 and the increase in catalytic activity to the anodic reaction of H_2.

For environmental monitoring applications, the sensor was examined also in 20 vol.% O_2 and the cross sensitivity toward different gases is given in Table 1. As can be seen from this result, the developed sensor is capable of generating a sensitive and selective response (Δemf) toward 100 ppm H_2 (about -600 mV) with smaller or negligible responses toward other examined gases.

In addition, the dependency of sensitivity on the H_2 concentration was examined. The almost linear relationship between the sensitivity and H_2 concentration was observed in the low concentration range (<100 ppm). On the other hand, in the higher H_2 concentration range (>100 ppm), a linear relationship was observed between sensitivity and concentration on logarithmic scale.

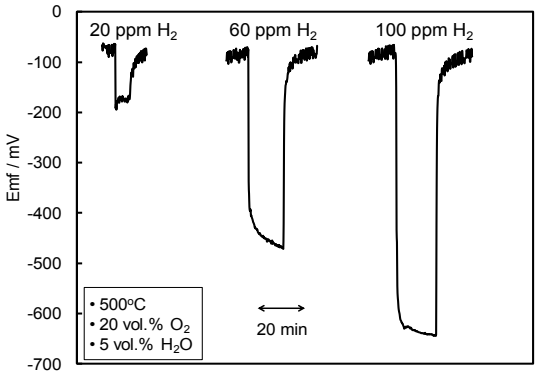

Fig. 3 The response transients of the sensor utilizing ZnO(+ 84 wt.%Ta2O5)-SE toward 20, 60 and 100 ppm H2 ; at an operating temperature of 500oC under humid conditions.

Figure 3 shows the response transients of the sensor utilizing ZnO(+ 84 wt.% Ta_2O_5)-SE toward 20, 60 and 100 ppm H_2 at 500°C under humid conditions (5 vol.% H_2O + 20 vol.% O_2). The 90% response time (t_{90}) to 100 ppm H_2 for the sensor was approximately 70 s. Considering these obtained sensing performances of the developed sensor utilizing ZnO(+ 84 wt.% Ta_2O_5)-SE, this device could be considered as one of prospective candidates for H_2 sensor capable of operating at high temperatures

Conclusions

A systematic investigation of effect of Ta_2O_5 addition into ZnO-SE on the resulting crystal structure as well as gas sensing performance was performed. It was observed that, the addition of 84 wt.% Ta_2O_5 into ZnO formed an entirely new phase of $ZnTa_2O_6$. The sensor using $ZnTa_2O_6$-SE was capable of generating highest response toward H_2 when compared with other SEs with different Ta_2O_5 additions. The study revealed that after 50 days, the response of the sensor using $ZnTa_2O_6$-SE toward 400 ppm H_2 was stabilized at around -840 mV, and was accompanied by negligible response toward other gases (Δemf < 80 mV). The sensitivity was found to have an almost linear relationship with H_2 concentration in the range of 10-100 ppm.

Acknowledgements

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