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Enhanced Response of High Temperature H_2 Sensors via the Application of Micro-dimensional Gold Mesh

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Abstract:

The authors present the sensing characteristics of a selective high-temperature YSZ-based H_2 sensor, with low sensitivity towards the following interfering gases: CO, CH_4, C_3H_6, C_3H_8, NO, NO_2 and NH_3. The developed H_2 sensor was highly sensitive with a lower detection limit of 10 ppm under standard atmospheric conditions (21 vol.% O_2, ≈32% RH at 25°C), making it an interesting potential candidate for environmental or safety monitoring applications. The fabricated sensor utilizes an Au mesh over the Pt sensing electrode to augment H_2 sensitivity; this enhancement will be discussed with respect to sensing electrode composition.

Key words: H_2, gas sensor, YSZ, Au mesh

Introduction

Despite the advances that functional nanomaterials have afforded the research community, many nanomaterials often undergo catastrophic changes during repeated excursions into high-temperature or harsh environments. Particularly, sensors utilizing Au micro/nano particles can exhibit strong aging effects due to particulate agglomeration and recrystallization at high temperatures [1]. These phenomena often result in degradation and detract from the positive effects that Au micro/nano particles can have on the sensitivity, selectivity, and augmented performance in gas sensors [2,3]. Rather than rely on a traditional method to co-deposit or cover an electrode with Au particles, in this work we present an alternative method with aspirations of creating a highly sensitive hydrogen (H_2) sensor via the application of robust Au micro-dimensional meshes. Reported herein is a study of the application of this mesh and a detailed examination of the sensing characteristics of a high-temperature YSZ-based electrochemical H_2 sensor capable of operating at 500-600°C with a lower detection limit of 10 ppm under standard atmospheric conditions (21 vol.% O_2, ≈32% RH at 25°C).

Experimental

Sensors were fabricated by separately screen-printing a sensing electrode (SE) and a reference electrode (RE) onto opposite sides of a YSZ substrate (10×10×0.5 mm, Nikkato, Japan). The pastes used for the SE (Pt:TR-7601, Au:TR-1301) and RE (Pt:TR-7905) were supplied by Tanaka Kikinzoku (Japan) and were used without further modification. After calcination of the screen-printed electrodes, the patterned SE was lightly coated with α-terpineol and then four Au TEM-grids (400 mesh, Gilder Grids, England) were deposited onto the coated SE. This was then dried at 130°C for 10 min, and calcined at 1000°C for 2 h. Finally, the sensor was bonded with Pt wire and Pt paste, and the assembled sensor was calcined at 1000°C for a further 2 h, finalizing the fabrication process. The specifications of the Au grids used and a photograph of a fabricated sensor are presented in Fig. 1(a) and (b), respectively. The completed sensors were assessed in a sensing-performance evaluation system, as described elsewhere [4]. The sensing signal was recorded as the electromotive force (emf), measured between the SE and RE.

Results and Discussion

The final fabricated sensor (calcined at 1000°C for 4 h) was observed via a scanning electron microscope (SEM, 6340F, JEOL, Japan) to ascertain if the Au grids mechanically failed after repeated excursions to 1000°C, these images are presented in Fig. 2. As can be seen from these images, the individual 25 μm-wide

lattice segments of the Au grid remained largely unchanged after several high-temperature excursions. However, the lattice segments in contact with the Pt-SE structure appear to have partially melted after the fabrication process, as evidenced by slight segment thinning, and the appearance of a nodular surface morphology.

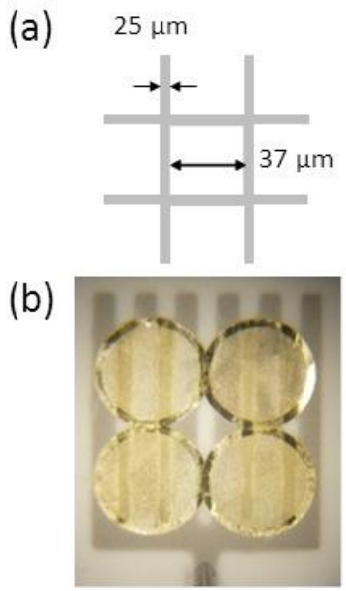

Fig. 1. (a) Mesh of the Au TEM grid; (b) photograph of Pt(+400 mesh Au grid)-SE.

In order to examine if the addition of an Au mesh over Au-SE or Pt-SE would affect sensitivity (Δemf) towards H_2, different Au mesh/electrode combinations were evaluated. These results are presented in Fig. 3 and indicate that the Au mesh (four 400 mesh Gilder grids) can greatly enhance H_2 sensitivity, when compared with the Pt-SE alone. The sensitivity of the Au-SE which was prepared for comparative purposes indicated that the presence of only an Au grid was insufficient to enhance H_2 sensitivity. Therefore, for all future experimentation a Pt-SE with four 400 mesh Au Gilder grids was used. It should be noted that 400 mesh Pt grids were not evaluated in this study, since they are not readily available.

The cross-sensitivity characteristics of the Pt(+400 mesh Au grid)-SE vs. a Pt-RE over an operational temperature range of 500-650°C is presented in Fig. 4. From this figure, it is evident that the cross-sensitivity characteristics of the Pt(+400 mesh Au grid)-SE favor selective H_2 sensing from 500-600°C, with some minor NH_3 sensitivity appearing at higher operational temperatures.

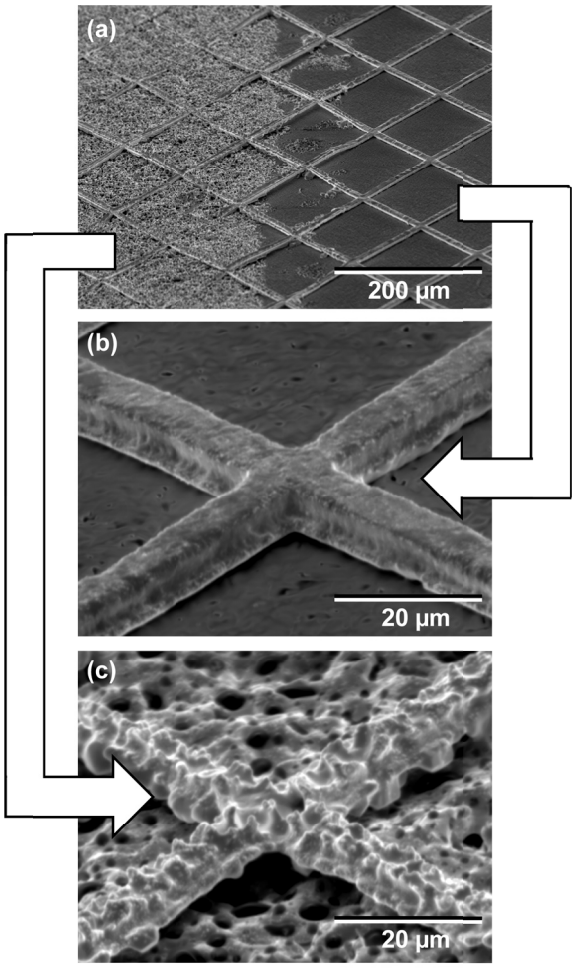

Fig. 2. SEM images of Pt(+400 mesh Au grid)-SE after fabrication (a) macro view of Au mesh over Pt-SE (left) and YSZ substrate (right), (b) Au grid over YSZ substrate, (c) Au grid over Pt-SE structure.

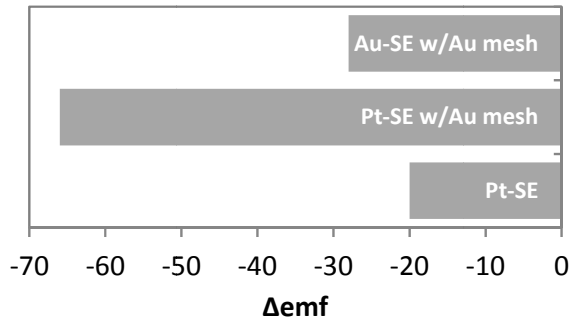

Fig. 3. H_2 sensing enhancement effect of Au mesh with varying electrode composition. Comparison conducted under the following conditions: 500°C, 21vol.% O_2, ≈32% RH at 25°C, 100 ppm H_2.

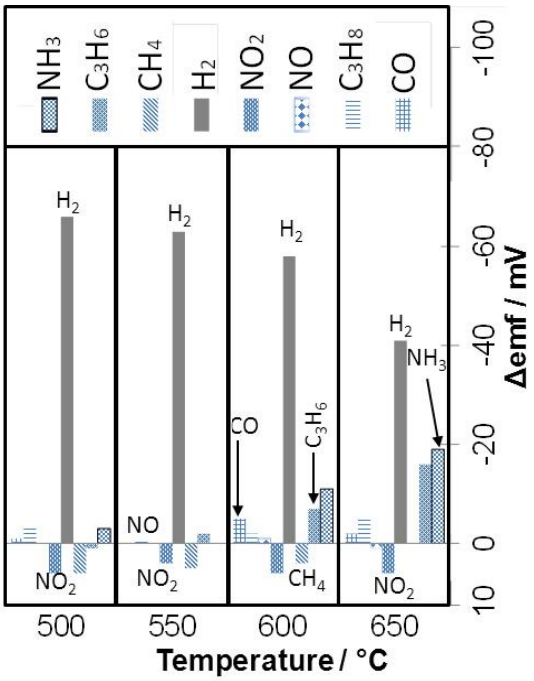

Fig. 4. Cross sensitivity of the sensor utilising Pt(+400 mesh Au grid)-SE and Pt-RE under the following operating conditions: 500-650°C, 21vol.% O_2, ≈32% RH at 25°C, 100 ppm target gases.

Closer examination of this sensor's performance is presented in Fig. 5. Here the emf response plotted against H_2 concentration exemplifies the enhancement capabilities of the Au mesh over layer, when compared with the Pt- SE. Over the examined concentration range of 10-100 ppm, the developed sensor exhibited an incrementally increasing rise in potential difference with H_2 concentration, although the response and recovery rates need to be further improved.

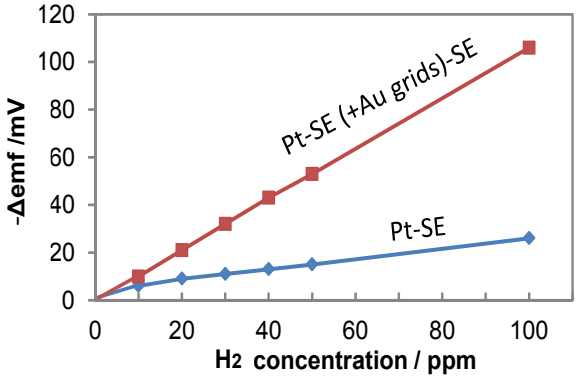

Fig. 5. H_2 concentration dependence of the sensitivity for the sensor using of a Pt-SE and Pt(+400 mesh Au grid)-SE under the following operational conditions: 500°C, 21 vol.% O_2, ≈32% RH at 25°C.

The SEM observations (Fig. 6) revealed that after 21 days of operation at temperatures ≥500°C that the mesh structure did not catastrophically fail, despite the high-temperature stress encountered during testing procedures. It can be seen that extended periods at elevated temperature have caused the Au lattice segments over the Pt-SE structure to broaden and recrystallize, occasionally resulting in a fractured segment. Whilst, the Au lattice segments over the YSZ substrate had only subtly changed, with the original well-defined edges visible in Fig. 2(b) becoming more rounded (Fig. 6(c)).

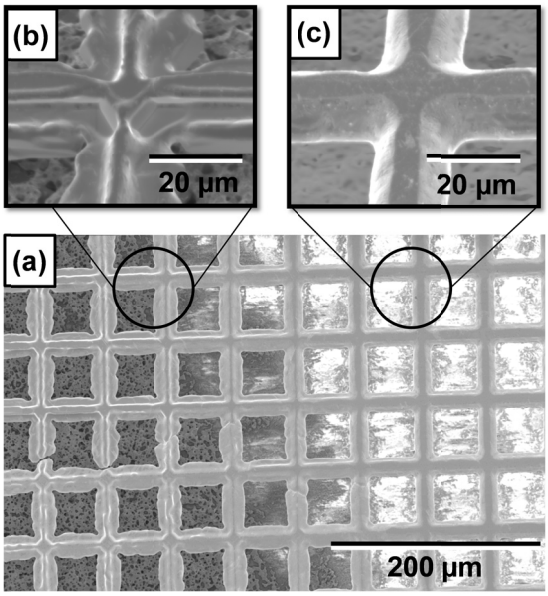

Fig. 6. SEM images of Pt(+400 mesh Au grid)-SE after 21 days at ≥500°C (a) macro view of Au mesh over Pt-SE (left) and YSZ substrate (right), (b) Au grid over Pt-SE structure, (c) Au grid over YSZ substrate.

The mechanical stability of the fine Au 400 mesh grids suggests that this Au mesh enhanced electrode structure may be suitable for harsh applications, however, further work is required to test the long-term stability of the present sensor. Additionally, the sensing mechanism behind the enhanced H_2 sensitivity of the Pt(+400 mesh Au grid)-SE warrants further investigation.

Conclusions

The addition of an Au mesh over a Pt-SE was found to be an effective method to augment the H_2 sensitivity of a YSZ-based sensor utilising a Pt-SE. The developed sensor exhibited low cross-sensitivity characteristics towards several different interfering gas species, and was capable of selectively and sensitively detecting H_2 at concentrations as low as 10 ppm over an operational temperature range of 500-600°C. The Au mesh, in the form of four 400 mesh TEM grids, was a convenient and consistent method to enhance H_2 sensitivity of a Pt-SE. Despite several excursions to temperatures as

high as 1000°C, the Au mesh retained its square lattice motif. The characteristics of the developed sensor make it an interesting potential candidate for environmental or safety monitoring applications.

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