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A Gold Nanoparticle/Polyaniline Nanofiber Sensor for Detecting H_2S Impurity in Hydrogen Fuel

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Abstract

Monitoring the concentration of H_2S in hydrogen fuel is an effective way to prevent the catalysis poisoning of solid oxide-fuel cells (SOFCs). In this study, a chemiresistive sensor based on gold nanoparticles (AuNPs) decorated polyaniilne (PANI) nanofibers was developed to detect the H_2S impurity in hydrogen fuel. A template-free electrochemical polymerization method was adopted to prepare the PANI nanofibers with horizontal orientation on the insulating gap area of an interdigitated electrode. The decoration of AuNPs on the PANI nanofibers was realized using the redox reaction between $HAuCl_4$ and PANI (emeraldine salt). A dehumidifier flowing system was designed to exclude the interference from the moisture in the hydrogen fuel. A high sensitivity (55% $\Delta R/R_0$) was obtained on 5 ppm H_2S in humidified H_2 stream, which indicates a potential application of the developed nanosensor in SOFCs.

1. Introduction

It is well known that H_2S contained in the fuel gases of SOFCs will cause degradation of fuel electrodes and thus electrochemical performance [1]. The contamination of sulfur compounds mainly derives from the preparation process of fuels due to the high sulfur concentration in source materials. Although great efforts have been made to desulfurize fuels as well as increase the sulfur-tolerance of SOFCs, H_2S poisoning is still a problem demanding prompt solution. The development of a sensor capable of monitoring the H_2S concentration in fuels is an effective alternative to prevent the sulfur poisoning in SOFCs. However, limited by the strict measurement environment of fuel stream, such as high H_2 concentration, high humidity and O_2 absence, H_2S sensor in fuel cell application is not available up to now.

The application of conducting polymers with one-dimensional nanostructures as gas sensors has attracted great interest during recent years owning to the reduced dimensionality, high aspect ratio, and unique electron transport properties. In comparison with conventional sensors, the gas sensors made of nano-CPs show improved performance such as high sensitivity and rapid response. Moreover, recent development in nanotechnologies makes conducting polymer nanowires or nanofibers easy to be fabricated and modified, which endows nano-CPs with new functions and applications. The present paper reports the preparation of a gold nanoparticles/polyaniline nanofiber sensor and its application in the filed of fuel cell for the detection of H_2S in hydrogen fuel.

2. General Instructions

2.1 Preparation of PANI nanofibers electrode

The PANI nanofibers were prepared according to a galvanostatical polymerization method reported in our previous work [2,3]. This method is characterized by a template-free electrochemical deposition of aniline on an interdigitated electrode treated with a silane-coupling agent (3-amino propyltriethoxysilane). The purpose of the surface modification is to tune the surface character (for example contact angle) of the insulting gap area and thus to obtain expected nanostructures and orientations of PANI. When suitable conditions (such as a current of 3μA and a time of 30 min) were applied, the polymerization resulted in a monolayered, horizontally oriented nanofiber network on the insulating gap area (as shoen in Fig.1). The green color of the film indicates that PANI obtained is in the form of protonated emeraldine salt. The horizontal orientation of nanpfibers has been proved helpful for enhancing the sensitivity of the chemiresistive sensors because the resistance is measured in the direction parallel to the substrates.

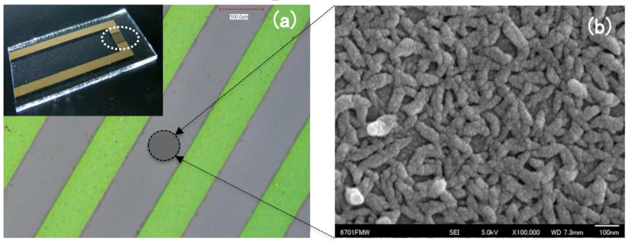

Fig. 1 SEM images of PANI nanofibers deposited on an interdigitated electrode to form resistive junctions.

2.2 Decoration of AuNPs on the PANI nanofibers

AuNPs were decorated on PANI nanofibers by immersing the PANI electrode in a solution of 5mM $HAuCl_4$ in HCl for 6 h. The reaction is based on the initial reduction of $AuCl^-$ anions by the emeraldine structure to form Au^0 nuclei as well as the subsequent autocatalytic growth of AuNPs as shown in Fig.2 [4]. The direct observation of AuNPs decorated on PANI nanofibers by SEM failed due to the small size of AuNPs (generally < 2nm). In view of their ultrafine structure and negative charge, it is considered that the AuNPs were decorated on the PANI nanofibers as the form of dopants.

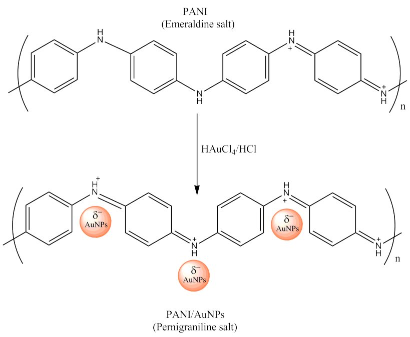

Fig. 2 Schematic diagram for the formation of AuNPs on PANI nanofibers. Partial emeraldine structure of PANI was oxidized to pernigraniline and $AuCl_4^-$ ions were reduced to ultrafine AuNPs, which were decorated on the PANI nanofibers as negatively charged dopants.

2.3 Experiment setup for the H_2S sensing in hydrogen fuel

Fuel cells are generally operated under a high temperature and high humid environment. Although nano-PANI has been an excellent candidate material for gas sensor application, the response of PANI sensor will be suppressed seriously by moisture. In order to exclude the interference of moisture, we designed a gas sensing setup as shown in Fig.3 to meet the online detection of H_2S in humidified fuel stream. A commercialized membrane type dryer tube was adopted to dehumidify the water vapor generated by bubbling.

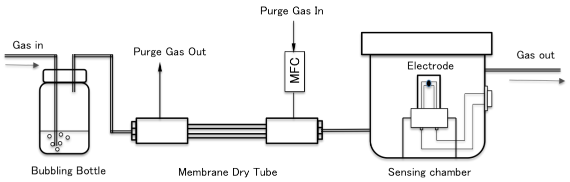

Fig.3 Schematic diagram of experiment setup for the gas sensing.

2.4 Dehumidifying effect of the membrane type dryer tube

The dryer is made from a fluorine containing, ion-exchange polymer that has high affinity for water molecules. The dehumidifying mechanism is based on the continuously transferring moisture through the membrane in the direction of the lower concentration (Inset of Fig. 4). A humidity sensor was set in the sensing chamber to evaluate the dehumidifying effect of the membrane type dryer tube. It can seen from Fig.4 that the high humid gas flow could be dehumidified to a relative humid less than 10%.

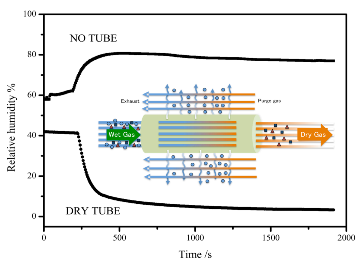

Fig. 4 Relative humidity of gas flow in the absence and presence of the dry tube.

2.5 H_2S sensing character of AuNPs/nano-PANI sensor

Fig. 5 shows the responses of PANI and AuNPs/PANI sensors on H_2S in humidified hydrogen when the dryer tube was used or not. The PANI sensor shows unobvious response on H_2S in H_2 both in the humidified and dehumidified cases due to the weak acid effect of H_2S. For the AuNPs/PANI sensor, its response was almost completely inhibited by the humidity. But after the dehumidifying treatment with the dryer tube, a high sensitivity with 55% $\Delta R/R_0$ was obtained. The response is attributed to the doping effect caused by the release of protons from the reaction between AuNPs and H_2S.

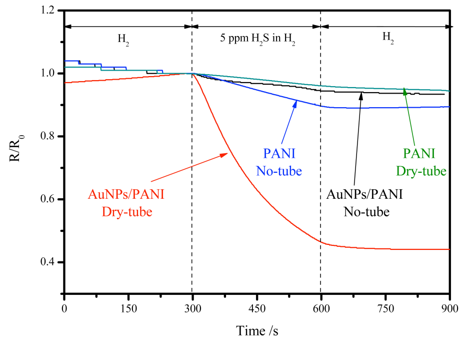

Fig. 5 Responses of PANI and AuNPs/PANI sensors on H_2S in humidified hydrogen in the absence and presence of dryer tube.

Conclusions

An AuNPs/PANI nanofiber sensor was prepared and its response characters on H_2S in humidified H_2 fuel was investigated. The results indicate that the developed nanosensor together with the designed dehumidifying setup is promising for the online monitoring of H_2S in H_2 fuel and thus to prevent the catalysis poisoning of SOECs.

Acknowledgements

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