

High Performance Potentiometric Sensor for Monitoring High Concentration Hydrogen Based on Pd-Pt Composite Electrode

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Summary:

A potentiometric high concentration hydrogen sensor including a Pd-Pt composite electrode was fabricated by combining a Pt electrode and a Pd nanoparticle layer. The hot-pressing method was used to manufacture a multilayer structure of Pt electrode/Nafion electrolyte/Pt electrode. Pd nanocolloids were synthesized using Pd powder and a solvent, and then coated on the upper Pt electrode to form a Pd nanoparticle layer. The fabricated sensor showed a fast and stable response in the hydrogen concentration range of 70 to 100%, enabling monitoring of hydrogen fuel used in fuel cell vehicles.

Keywords: hydrogen sensor, palladium, nanoparticle, composite electrode, fuel cell

Introduction

Net-zero carbon emissions policies enhance the development of hydrogen-related technologies. Detecting hydrogen leaks and measuring hydrogen concentrations are essential for hydrogen production, storage, and transportation [1]. Current hydrogen sensor technology focuses on detecting hydrogen leaks at the ppm level. However, it is not suitable for accurately monitoring high concentrations of hydrogen gas. In particular, hydrogen sensors to accurately measure the hydrogen concentration in hydrogen fuel cell vehicles, which ranges from 70 to 100%, have not been commercialized [2].

There are various types of hydrogen sensors, including metal oxide sensors, piezoelectric-based sensors, gas chromatography, and electrochemical sensors. Among them, electrochemical sensors are highly promising for practical applications due to their relatively simple structure and low power consumption. Electrochemical sensors consist of an electrode-electrolyte-electrode multilayer structure, and the catalyst within the electrode accelerates the electrochemical process. Palladium (Pd) can be used as another catalyst material together with platinum (Pt), the leading catalyst material, because hydrogen dissociation occurs on the Pd surface with a minimal activation energy barrier. Thus, in this study, we fabricated a composite catalyst electrode structure by adding a Pd

nanoparticle layer to the conventional Pt catalyst electrode. Its impact on the performance of potentiometric electrochemical sensors was examined by manufacturing high concentration hydrogen sensors. The resulting sensor exhibited a more stable response to high concentrations of hydrogen, compared to the sensor containing only the Pt catalyst.

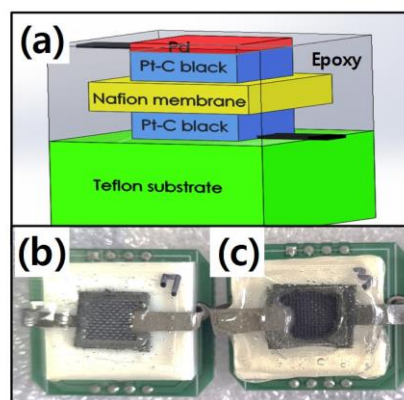


Fig. 1. (a) Schematic diagram of a high concentration hydrogen sensor with a Pd-Pt composite electrode. (b) Plan-view image of a fabricated hydrogen sensor with conventional Pt electrodes (no Pd nanoparticle layer). (c) Plan-view image of a fabricated hydrogen sensor with a Pd-Pt composite electrode.

Experimental

The Pd nanocolloid solution was prepared by mixing Pd powder and methyl isobutyl ketone solvent. Pd and methyl isobutyl ketone were

transferred to a cleaned small vial and stirred at 20 rpm for 20 min to produce a 2 wt% Pd solution. The hot-pressing method was adopted to fabricate the hydrogen sensor. A multilayer structure of Pt electrode/Nafion electrolyte/Pt electrode was manufactured under the hot-pressing conditions (temperature, time, pressure) of 60 °C, 60 sec, and 2 Mpa. The Pt electrode containing carbon paper coated with Pt-carbon black were purchased from a commercial material supplier (NARA Cell Tech). In order to form external terminals, metal tape was attached to the upper Pt and lower Pt electrodes, and the multilayer structure was sealed with epoxy, excluding the surface of the upper Pt electrode. The hydrogen sensor was completed by applying Pd solution on the Pt electrode and drying it.

Results

Fig. 1(a) shows a schematic diagram of a high concentration hydrogen sensor with a Pd-Pt composite electrode. The epoxy separates the lower counter electrode from the outside, allowing only the upper working electrode to respond to hydrogen. Fig. 1(b) and 1(c) show the hydrogen sensors manufactured using conventional Pt electrodes and a Pd-Pt composite electrode, respectively. As shown in Fig. 1(c), the color of the upper electrode appears dark black due to the coating of a Pd nanoparticle layer on a Pt electrode.

The hydrogen sensor operates based on the principle of a concentration cell. The hydrogen sensor is divided into a working electrode exposed to high concentration hydrogen gas and a counter electrode separated from the outside with epoxy. Since hydrogen dissociation occurs actively in the working electrode, hydrogen concentration can be measured by the electromotive force generated by the difference in hydrogen activity between the two electrodes.

Fig. 2(a) shows the voltage response of a hydrogen sensor employing only Pt electrodes, periodically exposed to pure hydrogen and nitrogen gases. When the sensor is exposed to pure hydrogen gas (100% H₂), significant fluctuations, in which the voltage drops to approximately -20 mV and then increases rapidly, occur. Fig. 2(b) shows the voltage response of a hydrogen sensor employing a Pd-Pt composite electrode. Unlike the previous result in Fig. 2(a), no fluctuations are observed and the sensor shows a stable voltage response. Pd activates the adsorption of oxygen ions, resulting in the reaction of hydrogen and oxygen ions to form H₂O [3]. Oxygen ions are formed from residual oxygen gas in the sensor measurement system. Thus, the use of Pd is thought to prevent voltage fluctuations by reducing a transient

overshoot in hydrogen ion concentration during hydrogen injection. The T90 response time of the sensor is very fast, less than 10 seconds.

Fig. 3(b) shows the voltage response of a hydrogen sensor for a gas mixture of 70% hydrogen and 30% nitrogen (70% H₂). The electromotive force at a hydrogen concentration of 70% is smaller than that at a hydrogen concentration of 100% (Fig. 3(a)), and the electromotive force difference for the two concentrations is 11.6 mV. This indicates that hydrogen gas in fuel cell vehicles with a concentration ranging from 70 to 100% can be effectively monitored using the hydrogen sensor based on Pd-Pt composite electrode.

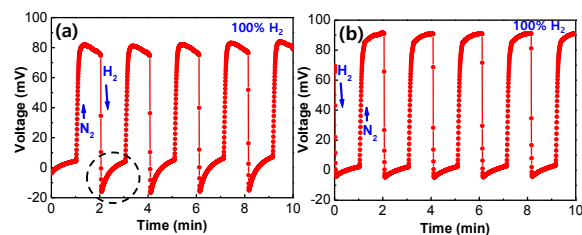


Fig. 2. Response curves of hydrogen sensors with different electrodes: (a) conventional Pt electrodes, (b) Pd-Pt composite electrode.

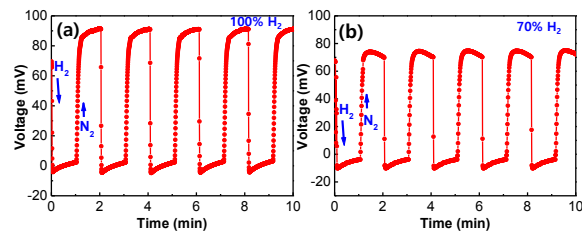


Fig. 3. Response curves of a hydrogen sensor with a Pd-Pt composite electrode, exposed to different hydrogen concentrations: (a) 100%, (b) 70%.

References

- [1] T. Hübert, L. Boon-Brett, G. Black, U. Banacha, Hydrogen sensors – A review, *Sensors and Actuators B* 157, 329-352 (2011); doi: 10.1016/j.snb.2011.04.070
- [2] Y. Liu, Y. Lei, X. Mao, H. Qian, H. Wen, S. Xia, Y. Xiang, Q. Chen, B. Xie, J. Hu, Wide-concentration-range hydrogen sensing using palladium-loaded SnO₂ nanoparticle films and understanding of hydrogen concentration-dependent sensing mechanism, *International Journal of Hydrogen Energy* 62, 783-793 (2024); doi: 10.1016/j.ijhydene.2024.03.037
- [3] J. Park, J. Yoon, Humidity dependence removal technology in oxide semiconductor gas sensors, *Journal of the Korean Institute of Electrical and Electronic Material Engineers* 37, 347-357 (2024); doi: 10.4313/JKEM.2024.37.4.1