Hydrogen Gas Sensing Properties of Calcium Metaphosphate Glass-derived Hydrogels

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A calcium metaphosphate glass-derived hydrogel shows high electrical conductivities of about 1 mS/cm around room temperature. Potentiometric hydrogen gas sensors using the hydrogel showed good Nernstian response to hydrogen gas concentration difference generated between detective and reference electrodes. The proton transport number of the hydrogel was estimated to be almost 1; no contribution of Ca^{2+} and OH^- ions in the hydrogel was shown. The evaluation of amperometric hydrogen gas sensors showed that limiting currents vary with hydrogen gas flow rates.

Among a variety of hydrogen sensors, electrochemical hydrogen sensors are currently attractive devices for their unique merits. For example, the sensors can operate at ambient temperature and be light in weight, thus allowing miniaturization. It is necessary for the development of high-performance electrochemical sensors to prepare an electrolyte with high proton conductivities. Proton-conducting Nafion® membranes have been widely used in the sensors and fuel cells.[1,2] The membranes still have some problems for practical use because of chemical and mechanical degradation during prolonged usage. In order to solve the problems, some high proton-conducting membranes consisting of stable inorganic compounds have been actively researched.[3–5]

When some kinds of phosphate glass powders are mixed with water, the mixture of the glass powders and water is completely converted into a viscous hydrogel in a few days.[6,7] After mixing water, the breaking of long phosphate chain structure in the powders occurs owing to hydration, and water goes into space between the phosphate chains to form the hydrogel. The hydrogels were reported to have numerous water and phosphate groups and thus show high electrical conductivity of about 1 mS/cm around ambient temperature.[6] The hydrogels are not only mechanically ductile but stable inorganic materials. The possibility for electric double-layer capacitors (EDCs) utilizing high conductivity of the hydrogels has been discussed.[7] The EDC performed higher voltage retentionability for self-discharge behavior after charging at constant voltage using the hydrogel than that using the H_3PO_4 solution. Since the hydrogels are supposed to be a proton conductor, an application to fuel cells has been examined. At this stage, the maximum power density of the fuel cell using the hydrogel was estimated to be $\approx 160\,mW/cm^2$ in our earlier report.[8]

In the present work, proton transport number of calcium metaphosphate glass-derived hydrogel was estimated by the potentiometric hydrogen gas sensors[9,10] utilizing the electromotive force (EMF) generated between two electrodes. Moreover, the possibility for the amperometric hydrogen gas sensors[10,11] using the hydrogel was investigated. Constant voltage is applied between the electrodes of the amperometric hydrogen gas sensors, and potential difference between the electrodes is generated. When hydrogen gas is supplied to one side of the electrodes in the sensor, protons in the electrolyte move to another electrode by hydrogen pumping ability of the sensors; oxidation or reduction reaction occurs at the each electrode. According to this reaction, limiting currents depending on hydrogen gas concentration are detected. As a result, the gas sensing can be performed.[10,11] The amperometric hydrogen gas sensors are more accurate than the potentiometric hydrogen gas sensors because the limiting current increases linearly with increasing the gas concentration.[11]

$CaO{\cdot}P_2O_5$ glass was prepared using reagent grade chemicals such as $CaCO_3$ and H_3PO_4 (85% liquid). A batch mixture of $CaCO_3$ and H_3PO_4 was melted under air in a Pt crucible at 1300 °C for 0.5 h. The melt was poured onto an iron plate and quenched by pressing. The resulting glass was crushed below 10 μm in diameter. A mixture of the glass powders and distilled water was placed on a polystyrene dish. The dish was shielded with a polystyrene cover using vinyl tape for prevention from drying. The sample was held at ambient temperature for 3 days to obtain calcium metaphosphate glass-derived hydrogel. Calcium metaphosphate glass-derived hydrogel is denoted as CP gel.

The catalyst ink was prepared by mixing Pt/C powders (0.35–0.40 mg/cm^2), polytetrafluoroethylene (PTFE) (10 wt %), water and 2-propanol. The ink was painted onto a carbon paper electrode and dried at 100 °C for 3 h to remove the mixture of water and 2-propanol. The hydrogel was placed in a silica glass tube of 10-mm inner diameter and 3-mm height and sandwiched between two electrodes. Insulative epoxy resin filled the gap between the glass tube and electrode in order to protect the leakage of hydrogen gas. The evaluation of hydrogen gas sensor was performed in the sealed container. In evaluation of potentiometric hydrogen gas sensors, the electromotive force (EMF) generated between reference and detective electrodes was measured using a Solartron SI-1287 electrochemical interface as a function of the hydrogen gas pressure. Total gas pressure was constant at 1 atm using argon gas, and the gas flow rate was 100 mL/min. 1% hydrogen gas in argon balance was supplied to the reference electrode.

In evaluation of amperometric hydrogen gas sensors, 100% nitrogen gas was supplied to the reference electrode, and 100% hydrogen gas of the flow rate of 0–40 mL/min was supplied to the detective electrode applying at 0.7 V between the reference and detective electrodes. These gas pressures were constant at 1 atm. Limiting current generated between the reference and detective electrodes was measured using a Solartron SI-1287 electrochemical interface.

Figure 1 shows the EMF response of a potentiometric hydrogen gas sensor using CP gel upon changing partial pressure of hydrogen gas, measured at ambient temperature. When 1%

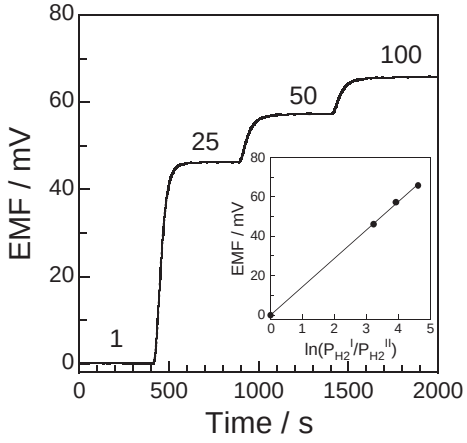

Figure 1. EMF response of a potentiometric hydrogen gas sensor using CP gel upon changing partial pressure of hydrogen gas, measured at ambient temperature. The inset shows the relationship between the EMF and the partial pressure.

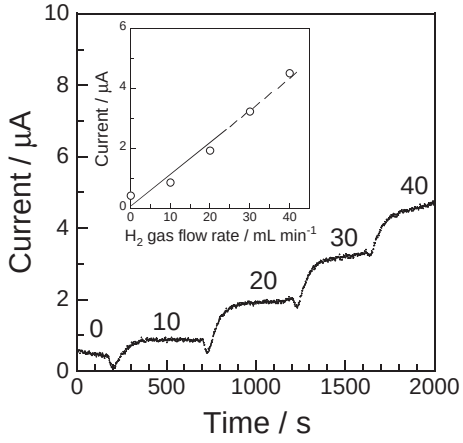

Figure 2. Amperometric response of a limiting current hydrogen sensor using CP gel upon changing hydrogen gas flow rate, measured at ambient temperature. The inset shows relationship between the limiting current and hydrogen gas flow rate.

hydrogen gas in argon balance was supplied to the reference electrode and hydrogen gas partial pressure at the detective electrode was changed from 1 to 100%, difference of hydrogen concentration between the electrodes was generated and the EMF was also generated. The EMF increased with increasing the partial pressure of hydrogen gas concentration and reached a steady level within 200 s.

Ideal oxidation and reduction of hydrogen at the detective and reference electrodes are $H_2 \rightarrow 2H^+ + 2e^-$ and $2H^+ + 2e^- \rightarrow H_2$, respectively. When ideal reaction occurred at each electrode, the number n in the Nernstian equation: $E = RT/nF \cdot \ln\{P(H_2^I)/P(H_2^{II})\}$, where F is Faraday's constant, R the gas constant, and T the absolute temperature, is shown to be 2. $P(H_2^I)$ and $P(H_2^{II})$ are partial pressures of hydrogen gas in electrode compartments of detective and reference, respectively. The number n was estimated using the equation to be 1.9. This value is close to a theoretical value of 2, indicating that the protons transfer through the CP gel. It was supposed that proton transport number of the CP gel are almost 1, and no contribution of Ca^{2+} and OH^- ions are shown. The proton conduction in the CP gel is suggested to be due to hopping of numerous protons dissociated from water and P–OH groups.[12]

Figure 2 shows the amperometric response of a limiting current hydrogen sensor using CP gel upon changing hydrogen gas flow rate, measured at ambient temperature. Hydrogen gas flow rate increased with increasing the limiting current. The limiting current reached a steady level within 200 s. Note the inset, which shows relationship between the limiting current and hydrogen gas flow rate; the limiting current depends proportionally on hydrogen gas flow rate since the proton transfer number of the CP gel is almost 1. The limiting current slightly decreased after changing the gas flow rate. Additionally, the limiting current slightly increased after reaching a steady level in the gas flow rate of 30 or 40 mL/min. These origins are not clear yet. Further investigations to clarify these origins are in progress.

The number n was estimated to be 1.9 from relationship between the hydrogen gas concentration and the EMF of a potentiometric hydrogen gas sensor using calcium metaphosphate glass-derived hydrogel. It was concluded that the proton transport number of the hydrogel is almost 1; the hydrogel can be used for the fuel cell electrolytes. The potentiometric and amperometric hydrogen gas sensors using the hydrogel could be operated. The response rate of the EMF and limiting current depending on hydrogen gas concentration was slow at this stage. We expect that the response rate can be improved after optimizing the electrode structure and shortening the distance between the electrodes of the sensors.

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