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Hydrogen Sensors

Hydrogen Gas Sensor Based on Proton-Conducting Clathrate Hydrate**

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Among alternatives to fossil fuels, H_2 gas is considered to be one of the most promising energy resources owing to its advantages of being nonpolluting and abundant in nature. In particular, fuel cells are currently receiving much attention for utilization of H_2 gas in the development of both stationary and mobile power generators. H_2 gas, however, inevitably has some safety concerns owing to the rapid energy conversion above its lower explosive limit of 4% in air. Accordingly, effective H_2 gas monitoring systems need to be developed to allow the safe application of various H_2-based energy devices. To this end, a number of analytical techniques have been developed in recent years to detect H_2 gas and determine its concentration.[1] Among them, electrochemical detection methods including both amperometric and potentiometric detection systems have received much interest. In these approaches, H_2 in inert gas (i.e. N_2 and Ar) or air is readily detected through the variation in current or voltage, even at low H_2 concentrations, and the systems can be simply designed for any dimensions.[2] These electrochemical sensors are generally composed of anodic and cathodic electrodes, where electrochemical reactions occur, and a proton conductor to receive and transport protons generated from the anode. However, for real applications, the main shortcomings of conventional electrochemical sensor systems, namely, the complicated fabrication procedure, poor stability, and high cost, should be overcome. As a potential method, we designed and tested a clathrate hydrate based hydrogen sensor.

Clathrate hydrates have been explored as a potential solid proton conductor because of their relatively high conductivities even at low temperature.[3,4] In particular, $Me_4NOH{\cdot}5H_2O$ has attracted much interest as a potential proton conductor because of its relatively high melting temperature (68 °C).[4] In comparison with widely used solid proton conductors such as polymer film and ceramic-based materials,[2] the real interest is placed on the technical and functional advantages that the icelike $Me_4NOH{\cdot}5H_2O$ offers. In this study, we seek to answer the following key issues: 1) Can we simplify the preparation procedure by directly using the raw reagent $Me_4NOH{\cdot}5H_2O$ itself, without any complex reactions or further treatments? 2) Is it possible to easily tailor the sensor to desired dimensions by synthesizing a bulk solid conductor by a crystallization process from a liquid state at room temperature? 3) Is the adopted clathrate hydrate material more cost-effective than conventional materials, including nafion products in particular? Even though these three main issues have been resolved, significant technical difficulties arising from the icelike features of clathrate hydrates remain for the fabrication of sensing devices. In particular, the catalytic electrode deposition procedure on the conductor is carried out in the organic solvent phase, which induces dimensional instability for $Me_4NOH{\cdot}5H_2O$. In full consideration of this problem, we suggest a new approach to fabricate a H_2 electrochemical sensor based on a clathrate hydrate. Utilizing the proposed approach, we successfully detected H_2 gas below the lower explosive limit in the amperometric mode using Pt catalyst loaded carbon electrodes. Notably, the suggested method does not require a deposition procedure of the Pt catalyst onto the conductor in the organic phase.

The fabricated sensor assembly in the present study is shown schematically in Figure 1. Well-dispersed Pt black in organic phase was coated with a brush uniformly on the surface of a carbon electrode, which was used as the anode. A pristine carbon electrode was used as the cathode. These two electrodes were connected to an ammeter. Liquid $Me_4NOH{\cdot}5H_2O$ was placed between the two electrodes, and subsequently solidified at room temperature for use as a proton conductor. As illustrated by the overall fabrication

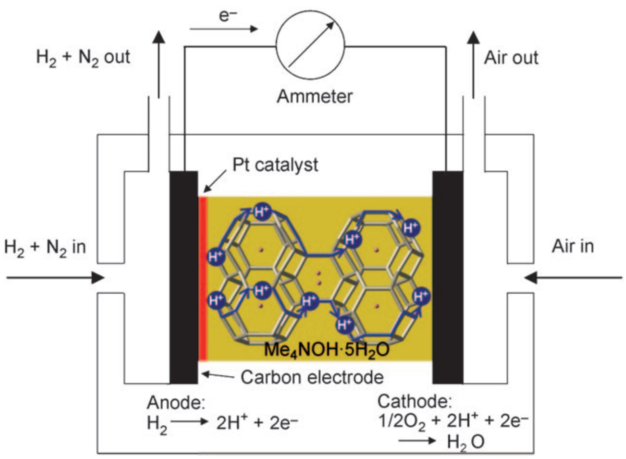

Figure 1. Diagram of the amperometric H_2 sensor assembly.

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procedure, a relatively simple and cost-efficient process can be realized by using an inexpensive reagent, namely, $Me_4NOH{\cdot}5H_2O$ clathrate hydrate, instead of a ceramic or nafion, both of which are widely employed in electrochemical sensors. In this device, good interfacial contact between the electrode and $Me_4NOH{\cdot}5\,H_2O$ was confirmed on the basis of the absence of any resistance other than the bulk resistance from the electrolyte in the impedance diagram (Figure S1 in the Supporting Information). The relatively high conductivity of $Me_4NOH{\cdot}5\,H_2O$, which is mainly due to active reorientation and hydrogen bonding breaking processes of water molecules,[3f,4a] could accelerate the transport of protons produced from the catalyst layers along the water framework. We of course expect that the Pt catalyst located on the interface plays a key role in the electrochemical reaction causing variation of current in the external circuit, which strongly depends on the crystallinity and particle size. In particular, a recent work revealed that the particle size and porous microstructure strongly influence the detection limitation of H_2 concentration and overall sensor performance.[5] Figure 2 shows distinct X-ray diffraction (XRD) peaks at around 40°, 46°, 68°, 82°, and 86°, corresponding to (111), (200), (220), (311), and (222) crystalline planes, respectively, of the Pt face-centered-cubic (fcc) lattice. The observed peaks for the Pt catalyst appear to be broad, compared with those of bulk state Pt, indicating the load of ultrasmall particles on the electrode.[6] Nevertheless, the peaks still reveal relatively high crystallinity. The average particle size was estimated according to Scherrer's equation to be around 8.8 nm from the width of the (111) plane peak. Under a well-loaded catalyst, few catalytic nanoparticles are detached from the carbon electrode in the organic solvent phase. Scanning electron microscopy (SEM) was used for observation of the surface morphology of the electrode. Figure 3 shows that Pt clusters with a size of several tens or hundreds of nanometers are well loaded between the carbon fibers. The surface morphology shows numerous pore openings between aggregated Pt particles extending deep into the inner structure connecting the pore networks. It can therefore be expected that the continuous pore interconnectivity leads to ready diffusion of H_2 to each catalyst layer. Additionally, the Pt nanoparticles might contribute to strong performance, providing a large number of reaction sites called triple-phase boundary, where the three important phases of electrolyte, gas, and catalyst are in contact.

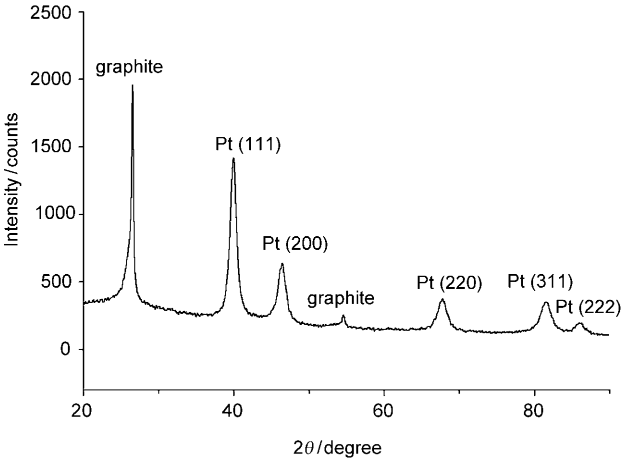

Figure 2. XRD pattern of Pt catalyst loaded carbon electrode. The graphite peaks arise from the carbon electrode.

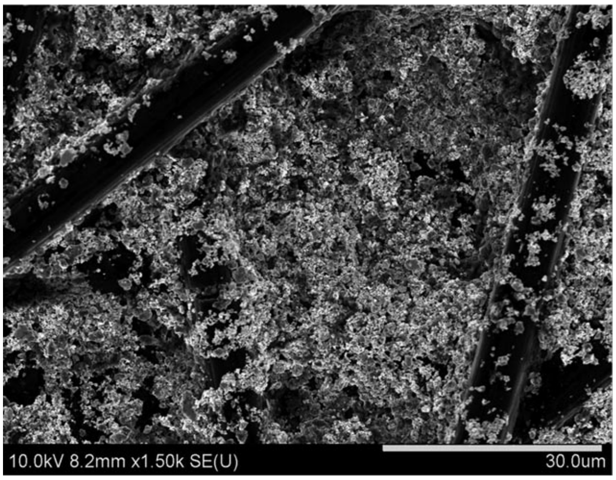

Figure 3. SEM photograph of the Pt catalyst on the carbon electrode at a Pt loading of $6.18\ mg\,cm^{-2}$.

In this electrolytic device, the main electrochemical process causing variation of current in the circuit is the oxidation reaction of H_2 molecules at the anode. The penetrated H_2 molecules into the interface between catalyst layer and electrolyte are split into the protons and electrons under an oxidation potential. The protons produced are transported through hydrogen-bonded $Me_4NOH{\cdot}5\,H_2O$ host framework, and an equivalent number of electrons are conducted to the carbon electrode and flow in an external circuit and react with the protons and O_2 molecules to form water molecules at the cathode (Figure 1). Accordingly, we can readily detect the existence of H_2 gas through simple observation of an increase in current. The amperometric responses were measured at 0.05 V for two representative concentrations of 10 and 1 % H_2 (balanced with N_2), and the results are shown in Figure 4. For the case of 10 % H_2 gas injection, the current instantaneously rose to its saturated value (Figure 4a). For the lower 1 % H_2 concentration, a similar step response was also observed, but the current gradually increased and reached a lower saturated value owing to the lower partial pressure of H_2 (Figure 4b). A signal level of 90 % was achieved within response times of 6 s and 20 s for 10 % and 1 % H_2, respectively. The present results indicate that the icy clathrate hydrate sensor shows sufficiently rapid response for hydrogen concentrations between 1 and 10 %. Meanwhile, the increased current was again lowered by cessation of the H_2 gas supply, immediately arriving at the base current level within 40 s. In contrast to the response patterns, the corresponding recovery times did not appear to be significantly influenced by the H_2 concentration. We further observed that the clathrate hydrates were not decomposed during a lengthy sensing test. Owing to this hydrate stability, the saturated current value at each cycle

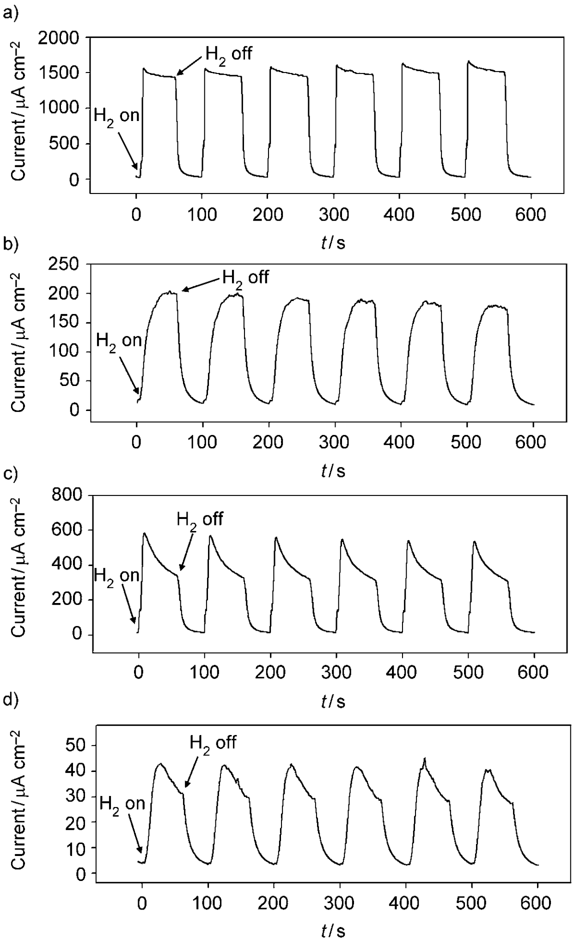

Figure 4. Step response behavior of sensor assembly with 6.18 mg cm^{-2} Pt catalyst for 10% H_2 (a) and 1% H_2 (b), and with 3.50 mg cm^{-2} Pt catalyst for 10% H_2 (c) and 1% H_2 (d) at room temperature.

could be maintained at almost constant level even after several dozen repeated H_2 exposures for long-term sensing tests and thus the sensing device could function within an allowable performance range (Figure S2 in the Supporting Information).

Catalysts affect reaction rates by lowering the activation energy, and therefore the response behavior strongly depends on the amount of Pt catalyst which provides the reaction sites, as well as desirable H_2 concentrations. For less-loaded catalysts, the resulting currents approach much lower saturated values when the corresponding electrochemical reactions proceed in both 10 and 1% H_2 concentrations (Figure 4c,d). However, their response times were almost identical to the values presented in Figure 4a,b. In spite of this favorable tendency of the catalyst effect, the chemical and physical pattern of Pt should be more precisely determined with a view to maximizing the triple-phase boundary for economical preparation of the sensor assembly. The applied voltage can also serve as a promoter in the electrochemical reaction by providing a more positive potential supply to the anode. The promotion effect is clearly shown at the low H_2 concentration of 0.1%, as the response time is considerably reduced when larger voltage is applied (Figure 5). However, slower response time and lower saturated current value still remain, relative to the results at higher H_2 concentrations. The relationship between the current output and H_2 concentration is depicted in Figure S3 in the Supporting Information. We further tested the sensing performance at −20 °C. Even at this lower temperature, the typical step responses were clearly observed, as shown from those measured at room temperature (Figure 6). This sensing behavior suggests that the hydrate-based H_2 sensor can be applied to even relatively low saturated current and slow response time owing to temperature-dependent proton conduction.

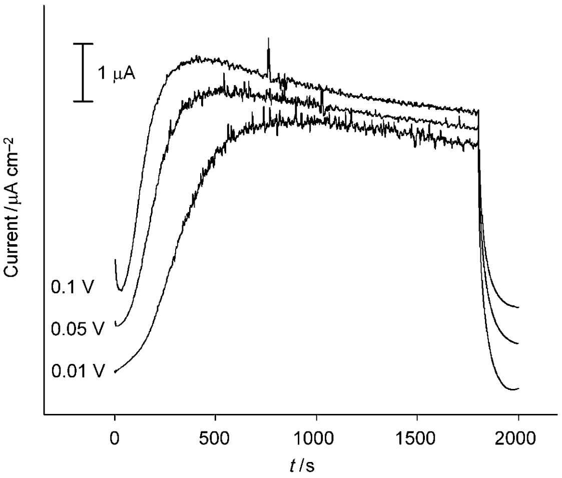

Figure 5. Step response behavior of sensor assembly with 6.18 mg cm^{-2} Pt catalyst for 0.1% H_2 in N_2 at room temperature.

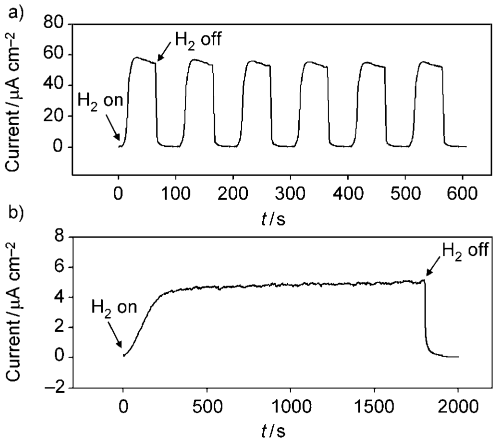

Figure 6. Step response behavior of sensor assembly with 6.18 mg cm^{-2} Pt catalyst for 10% H_2 (a) and 1% H_2 (b) in N_2 at −20 °C.

Subsequently, we examined the response behavior in the air + H_2 mixed gas system at close to real environmental conditions. As shown in Figure S4 (Supporting Information), its saturated current appeared to be considerably lower than that for N_2 + H_2 mixed gas[7] because of the additional reaction of H_2 with O_2,[2a,8] which is essentially identical to the trend reported by Miura et al.[9] However, a notable feature is that the fast and reproducible responses were monitored in the circuit, indicating that the present sensor assembly can be effectively used for the detection of H_2 gas below the lower explosive limit of 4% in air. However, for moisture-saturated $N_2 + H_2$ gas,[10] we detected response patterns and current values quite similar to those of the moisture-free $N_2 + H_2$ gas system (Figure S5 in the Supporting Information). These two additional tests indicate that the potential impurities might alter to a certain degree the current intensity, but do not significantly affect the sensing performance of hydrate-based H_2 sensor. We note that for stable operation, both an excess voltage and the chemical nature of the anionic species might affect the hydrate stability and the occurrence of hydrate structure decomposition. For $HPF_6{\cdot}6H_2O$[11] and $Me_4NF{\cdot}4H_2O$,[12] which possess melting temperatures above room temperature, typical response patterns are clearly shown at several sensing cycles for 10% H_2 concentration, but they are readily decomposed to the liquid state even at a short H_2 exposure time. This result indicates that the water frameworks built with H^+ or F^- ions can be destabilized by the penetrating protons, causing undesirable results for sensing performance.

Owing to desirable physicochemical characteristics of icelike $Me_4NOH{\cdot}5H_2O$, the sensor assembly shows good performance with fast response and recovery time, and requires a simple preparation procedure. The relatively high proton conductivity, even at low temperatures, can extend the practical sensor operation range. The present research provides a preliminary proof of concept and shows that special types of ionic clathrate hydrates can be effectively used as promising gas-sensor materials.

Experimental Section

Reagents: $Me_4NOH{\cdot}5H_2O$ (>97%, Aldrich), Pt black (99%, Alfa Aesar), isopropyl alcohol (>99.5%, Junsei), and 5 wt% nafion perfluorinated resin solution (Aldrich) were used as received. Water of ultrahigh purity was obtained from a Millipore purification unit. High-purity H_2 and N_2 mixed gases (10%, 1%, and 0.1% H_2) were supplied by Special Gas.

Preparation and measurements: Pt black as a catalyst for promoting electrochemical reaction was mixed with water, isopropyl alcohol, and 5% nafion perfluorinated resin solution. The mixture was then repeatedly stirred and dispersed by ultrasonification. The produced catalyst ink was uniformly coated with a brush on the surface of electroconducting carbon paper (SGL carbon group). The organic solvent was evaporated under ambient conditions. Carbon electrodes were loaded with 3.40 and 1.93 mg Pt over an area of $0.55 \times 1.0\,cm^2$ to test the behavior for different Pt loadings. Liquid $Me_4NOH{\cdot}5H_2O$ was placed between the anode and cathode in a teflon-coated cell and was subsequently crystallized at room temperature for at least 1 day. H_2 and N_2 mixed gases were injected into the anode at a flow rate of $200\,cm^3\,min^{-1}$ by using a Brooks 5850E mass-flow controller. The current variations in an external circuit connecting both electrodes were measured every 0.2 s using a Solartron 1260 impedance/gain-phase analyzer and a 1287 electrochemical interface at constant voltage and at room temperature. The impedance diagram was plotted over a frequency range from 10 to 10^6 Hz.

The XRD pattern of the Pt-loaded electrode was recorded on a Rigaku D/max-IIIC diffractometer with $Cu_{K\alpha}$ as a light source ($\lambda = 1.5406$ Å) at a generator voltage of 40 kV and a generator current of 40 mA. The crystal structure and particle size were determined by using the crystallographic analysis software JCPDS Card. SEM photographs were recorded on a HITACHI S-4800 instrument at a beam energy of 10 kV for examination of the surface morphology of the electrode.

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