Microtubular Hydrogen Electrode, a Reference Electrode for Electrochemical Analyses

Masayuki Kunimatsu,[b,c] Huan Qiao,[a] and Tatsuhiro Okada[a,z]

[a]*National Institute of Advanced Industrial Science and Technology, Ibaraki 305-8565, Japan*
[b]*New Energy and Industrial Technology Development Organization, Kanagawa 212-8554, Japan*

This paper describes a new type of miniature hydrogen electrode that is composed of a tubular polymer electrolyte and is suitable for use as the reference electrode in electrochemical measurements. The tubular hydrogen electrode was fabricated by supporting platinum black powder inside a perfluorinated polymer electrolyte tube and feeding hydrogen gas into the tube. It can be used as the reference electrode for electrochemical measurements both in acid electrolyte solutions and in a testing apparatus, for example, in polymer electrolyte fuel cells. The specific feature of the tubular hydrogen electrode is that it is so small that it can fit in microanalytical or electrochemical cell systems. The tubular hydrogen electrode can also work as both a counter electrode and a nonpolarizable reference electrode because of the very large specific surface area of the platinum particles deposited inside. This makes these tubular hydrogen electrodes usable in two-electrode cells, which is another advantage over conventional glass-type hydrogen reference electrodes.
© 2005 The Electrochemical Society. [DOI: 10.1149/1.1874732] All rights reserved.

Ordinary electrochemical measurements, such as steady-state voltammograms or cyclic voltammograms (CVs) are done with three-electrode cells consisting of a working electrode, reference electrode, and counter electrode. The reference electrode assigns the standard potential for the working electrode and is required for its stability and reproducibility, as well as the ease of installation to the measuring system.[1-3] The standard electrode potential of hydrogen electrodes has been defined as zero at all temperatures.[4,5] Although the hydrogen electrode is the best reference electrode for use in an aqueous solution because of its stability and reproducibility in wide temperature and pH ranges,[1-3] the saturated calomel electrode or silver silver-chloride electrode are frequently used as practical reference electrodes because of the ease of installation in the measuring system.[4]

However, there are problems in such electrodes, *e.g.*, occurrence of the liquid junction potential and contamination of the measuring system by salts leaching out of the inner reference solution of the electrodes. The large size (*ca.* 1 cm diam and 8-10 cm length) is also a disadvantage for microanalytical uses. A miniaturized and easy-to-use hydrogen reference electrode would make the electrochemical analyses easier and much more reliable.

Recently, we have developed a micro fuel cell with tubular polymer electrolytes and have made steady progress in our research and development.[6,7] In this microtubular fuel cell, the fuel chamber is the inside space of the tube, and there is no leakage of fuels, which has been a major problem for planar-type fuel cells. Thus, tubular electrolytes may offer an attractive basis for fabricating a new type of hydrogen reference electrode.

In this paper, we report the test results of a newly developed hydrogen electrode consisting of microtubular polymer electrolytes applied to electrochemical systems. We evaluated the following criteria: the effect of the acid concentrations of electrochemical systems on the potential, temperature-dependence characteristics, dynamic characteristics, especially response time to the condition change, and polarization characteristics for unexpected current flow. The viability of a two-electrode system is also examined, because a large platinum surface area is obtained by the use of platinum black particles inside the tube. As a practical example, the electrochemical measurement is carried out in a sulfuric acid solution while using a tubular hydrogen electrode as a reference electrode. The perspective of using a tubular hydrogen electrode as a reference electrode in testing polymer electrolyte fuel cells (PEFCs) is also presented.

Experimental

Fabrication of microtubular hydrogen electrodes.—Flemion tubes (inner diam 0.3 mm, outer diam 0.6 mm, perfluorosulfonic acid polymer electrolyte membrane, Asahi Glass Engineering) were used as polymer electrolytes, which were cleansed by successive boiling in 3 wt % H_2O_2, deionized (DI) water, 1 mol/L H_2SO_4, and DI water, each for 1 h. To prepare a hydrogen electrode, the platinum electrode layer was made by injecting Pt black catalyst paste into the electrolyte tube containing a current-conducting platinum wire of 0.2 mm diam. The catalyst paste was made by mixing Pt black powder (Johnson Matthey, Inc.) and 5 wt % Nafion solution (Aldrich) and stirring until the mixtures became a smooth paste. The tubular hydrogen electrodes were dried at room temperature and then heat-treated at 135°C for 3 min. A picture of a tubular hydrogen electrode is shown in Fig. 1.

Another type of fabrication was tested where the catalyst layer inside the tube was made by the chemical plating method (see the Appendix). Both Pt plating and a mixture of PtRu plating were tested as hydrogen electrodes.

Measurements with microtubular hydrogen electrodes.—The prepared tubular hydrogen electrode was evaluated in the electrochemical system shown in Fig. 2, by measuring the following characteristics in comparison with a normal hydrogen electrode. The items evaluated were (*i*) potential indication of the tubular hydrogen electrodes, (*ii*) effect of sulfuric acid concentrations of the outside solution, (*iii*) temperature dependence of the potential, (*iv*) time response, and (*v*) polarization characteristics. Hydrogen gas of more than 99.995% purity was fed inside the tubular
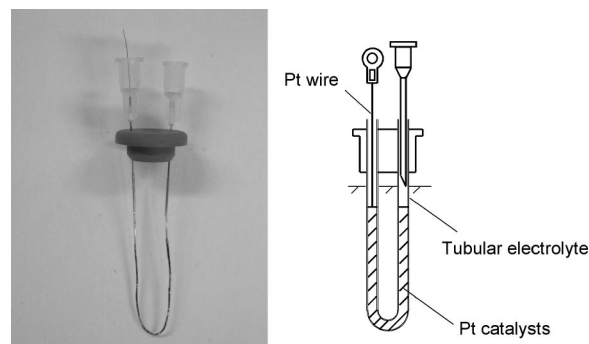
[c] Present address: Kanagawa Industrial Technology Research Institute, Kanagawa, 243-0435, Japan.
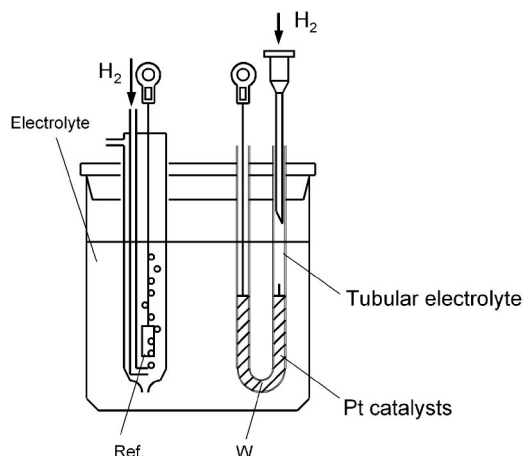[z] E-mail: okada.t@aist.go.jp

Figure 1. Photograph of a tubular hydrogen electrode.

Figure 2. Schematic of electrochemical cell used in this study.

Figure 4. Indication potential of tubular hydrogen electrode at various temperatures.

electrode at 1 atm pressure. Temperatures of the electrochemical cell were controlled by thermostat.

The reference hydrogen electrode (RHE) consisted of a glass tube with hydrogen inlet and outlet, platinum mesh to which the hydrogen gas was supplied in contact with sulfuric acid solution and the electric lead to the platinum mesh. The indication potentials were also examined in neutral and alkaline solutions. As applications, the tubular hydrogen electrodes were evaluated as reference electrodes not only in electrolyte solutions but also in fuel cell testing systems.

Results

Hydrogen electrode potential at tubular hydrogen electrode.—Figure 3 shows the time variation of the indication potentials of the tubular hydrogen electrode in sulfuric acid solutions of various concentrations. The stable potentials, which are within ± 0.2 mV of RHE, are attained in sulfuric acid in about 5 min. It is seen in Fig. 3 that the tubular hydrogen electrode completely works as an RHE.

Temperature dependences of potentials at tubular hydrogen electrode.—Figure 4 shows the potential of the tubular hydrogen electrode measured over time at each temperature. It indicates that a temperature increase leads to a negative shift of the indication potentials. The potential shifted in negative direction by 1.0 mV at 50°C and by 4.0 mV at 80°C.

Testing in neutral and alkaline solutions.—In addition to the testing in acid solutions as shown, testing was also carried out in
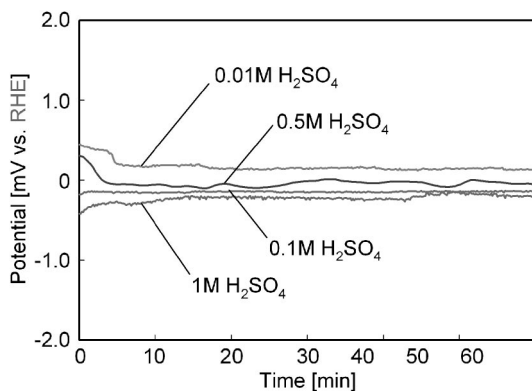
neutral and alkaline solutions. The indication potentials of tubular hydrogen electrodes in KOH and KCl solutions are shown in Fig. 5. The potentials considerably fluctuate from RHE in both solutions and do not stabilize. These potential fluctuations are probably due to the exchange of hydrogen ions in the polymer electrolyte tube by potassium ions in the solution. Cations except hydrogen ions were not to be used in the electrolyte solution. Therefore, it is concluded that tubular hydrogen electrodes that are defined as H^+ responding electrodes cannot be used in neutral and alkaline electrolyte solutions.

Dynamic response of tubular hydrogen electrode.—Figure 6 shows the CV of a tubular hydrogen electrode as a working electrode. This CV shows characteristic peaks of polycrystalline platinum, and the interference due to the impurity is not observed. The platinum surface area estimated from the adsorption or desorption peaks of hydrogen was 100 cm^2, approximately 700 times larger than the geometrical surface area. This fact indicates that a two-electrode system may be designed for electrochemical measurements by using the single tubular hydrogen electrode. In this case, a tubular hydrogen electrode works as both a reference electrode and a counter electrode.

As a test experiment of tubular hydrogen electrodes, the CV of a platinum plate was measured in sulfuric acid solutions. Figure 7 shows CVs measured with two-electrode and three-electrode cells when a tubular hydrogen electrode was used as the reference electrode and also as the counter electrode. The same results occurred with both the two-electrode and three-electrode cells, indicating the applicability of tubular hydrogen electrodes in simple two-electrode cells.
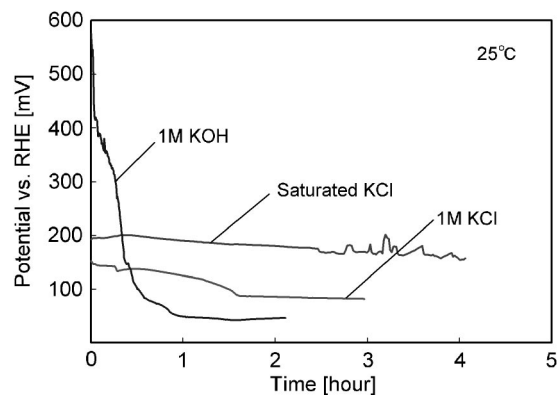

Figure 3. Indication potential of tubular hydrogen electrode in sulfuric acid solutions.

Figure 5. Indication potential of tubular hydrogen electrode in alkaline and neutral solutions.

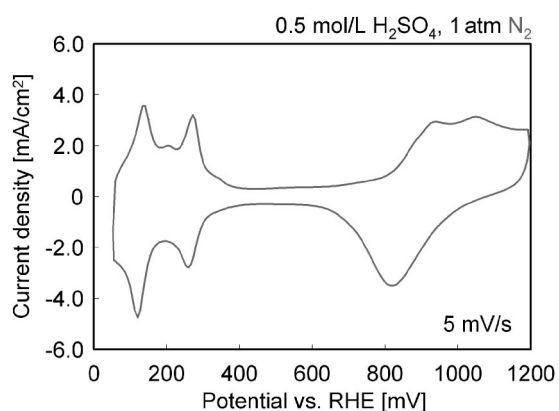**Figure 6.** CV of tubular hydrogen electrode.

Figure 8. Polarization curves of tubular hydrogen electrode.

Figure 8 shows the polarization characteristics when a current is forced to flow to the tubular hydrogen electrode. A gradient of 1.3 mA/(cm² mV) was obtained in a 0.5 mol/L sulfuric acid solution. When the ohmic drop was compensated for the electrolyte solution resistance with the current interruption method, a gradient of 2.9 mA/(cm² mV) was obtained. As such, tubular hydrogen electrode may be used in two-electrode electrochemical cells because the potential shift is so small that it can be neglected for measurements in a current range of a few milliamperes (*i.e.*, it can be regarded as a nonpolarizable electrode). In addition, hysteresis of the potential during the sweep is negligible.

Figure 9 shows the current response when potential steps are applied to the tubular hydrogen electrode. The potential immediately recovers to the initial potential when the current flow is stopped. No problems are observed in the response characteristics as long as the tubular hydrogen electrodes are used in normal electrochemical measurements.

Application to fuel cell measurements.—A tubular hydrogen electrode was installed in a PEFC (see the Appendix). The electrolyte membrane of the PEFC and a tubular hydrogen electrode were connected together by gluing with 5 wt % Nafion solution and heat-treated at 135°C. The potential difference between a tubular hydrogen reference electrode and a PEFC at both the anode and the cathode supplied with H_2 falls within ±0.2 mV. This means that the tubular hydrogen electrode functions as a reference electrode in PEFCs.

Figure 10 shows the result measured in a direct methanol fuel cell (DMFC) where the anode potential, the cathode potential, and

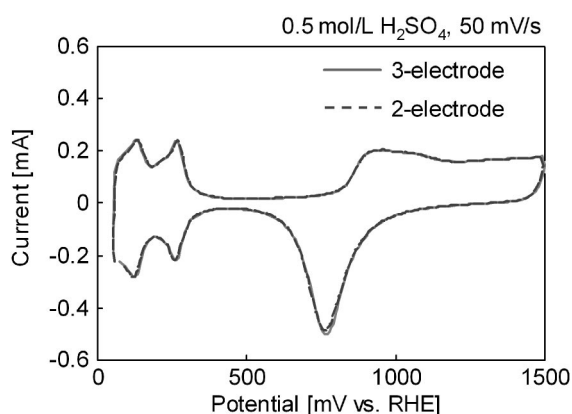the cell voltage were recorded separately. The tubular hydrogen electrodes performed perfectly and conveniently as the reference electrode in fuel cells.

Discussion

The fixed capacity of the ion-exchange groups, or the hydrogen ion concentration, in the polymer electrolyte corresponds to approximately pH 0 (*ca.* 1 mol/L H^+ concentration in the polymer electrolyte). Then it is expected that the microtubular hydrogen electrode would work as a standard hydrogen electrode (SHE) regardless of the H^+ concentration in the electrolyte solutions, if this solution has no other cations. In the case where there are other cations, the H^+ concentration at the inner surface of the tube would be regarded as constant in the experimental time until the cation penetrates the tube completely. If this is true, then the potential of the tubular hydrogen electrode in reference to RHE (glass electrode) should be expressed as follows

$$E = - \frac{RT}{F} \ln a_{H^+}(s) = - \frac{RT}{F} \ln c_{H^+}(s) \qquad [1]$$

where the activity $a_{H^+}(s)$ of H^+ in the solution is replaced by the H^+ concentration $c_{H^+}(s)$.

The indication potentials in sulfuric acid solutions of various concentrations are shown in reference to SHE (Fig. 11). Contrary to expectations, the performance as shown in Fig. 11 indicates that the tubular hydrogen electrode performs like an RHE.

RHE indicates the potential of a hydrogen reaction between H^+ ion in the electrolyte solution and the H_2 gas absorbed on the plati-

Figure 7. CVs of Pt plate measured with three-electrode and two-electrode systems using tubular hydrogen electrode.

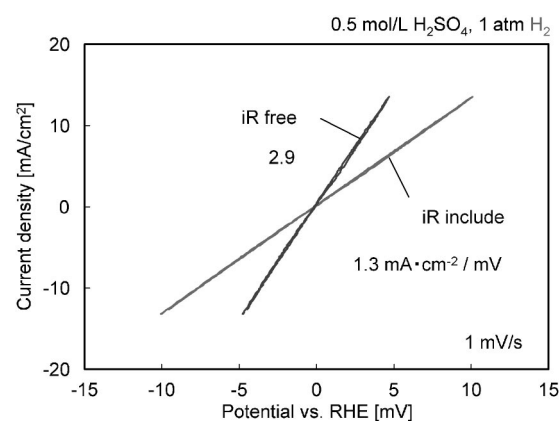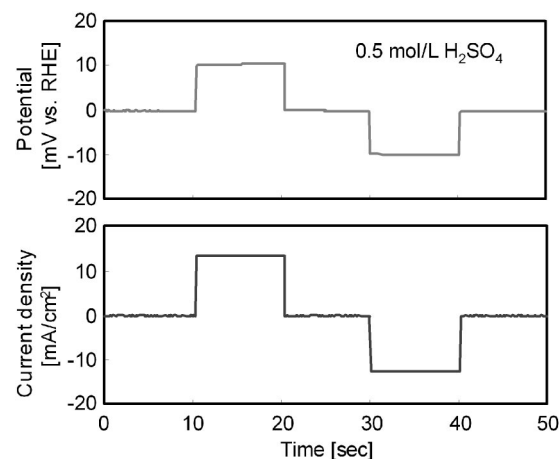**Figure 9.** Response characteristics of tubular hydrogen electrode.
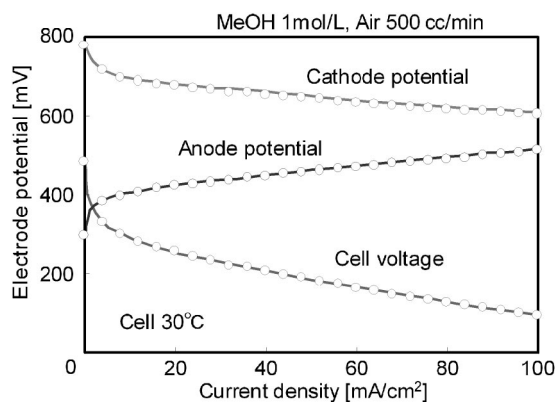
Figure 10. Polarization characteristics of a DMFC measured by using a tubular hydrogen electrode.

Figure 12. Indication potential *vs.* SHE with pH contour lines.

num surface contacting the same electrolyte solution. In the tubular hydrogen electrode, the hydrogen reaction occurs at the interface between the polymer electrolyte and the platinum particles contacting it, without direct contact to the solution outside of the tube. From the preceding results, it is conceived that the indicated potential may involve the junction potential between the polymer electrolyte and the outside electrolyte solutions,[8] because a hydrogen reaction always occurs on the platinum particle at the polymer electrolyte inside the tube. This junction potential E_{junc} is assumed to take the form

$$E_{junc} = \frac{u_+ - u_-}{u_+ + u_-} \frac{RT}{F} \ln \left\{ \frac{u_+ c_+(s) + u_- c_-(s)}{u_+ c_+(m) + u_- c_-(m)} \right\} \qquad [2]$$

Here u_+ and u_- are the mobility of cations and anions, respectively, that can transfer through the membrane/solution interface. m and s stand for the membrane phase and the solution phase at this interface. For cation exchange membranes like in the present case, $u_- = 0$ and Eq. 1 reduces to the Nernst potential

$$E_{junc} = \frac{RT}{F} \ln \frac{c_+(s)}{c_+(m)} \qquad [3]$$

Summing up Eq. 1 and 3 and setting $c_+(m) = 1$, the net potential becomes zero, which is what we observed in Fig. 3.

The indication potentials of conventional hydrogen electrodes should follow Nernst's equation for temperature changes. For the tubular hydrogen electrode, polymer electrolyte membranes may expand with the temperature increase so that it is necessary to calibrate the effect of the temperature. It seems that the concentration of the ion-exchange group of the polymer electrolyte decreases due to an
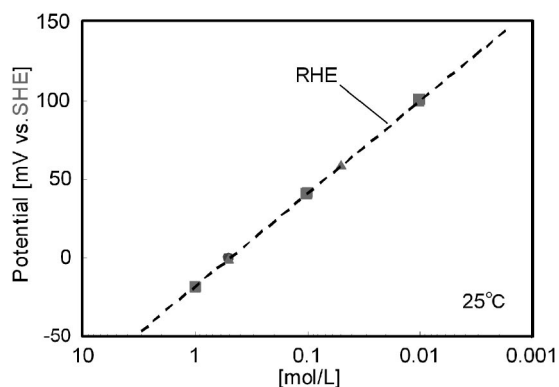
increase in water content by polymer swelling, while the size of the polymer electrolytes increases due to a temperature increase.

Figure 12 gives a pH contour line obtained from Fig. 4 for the temperature dependence of the potential. The pH contour is drawn from the following equation

$$E = E^0 + \frac{RT}{F} \ln a_{H^+} = - \frac{RT}{F} pH \qquad [4]$$

In Fig. 12, the apparent pH of the electrolyte increases with the temperature increase. This apparent pH increase would be in part due to the polymer swelling and decrease in the average concentration of ion-exchange sites. The potential of the tubular hydrogen electrodes shifts to the negative direction with the temperature increase (the potential decreases by 1.0 mV at 50°C) so that correction is necessary for accurate analyses.

There are several advantages in using a microtubular hydrogen electrode. First, the size of the tube is so small that it can be used in microanalytical cells and miniature-sized electrochemical systems. Second, there is no disturbance to the measuring system caused by hydrogen bubbling into the solution, which sometimes becomes a problem when conventional-type hydrogen electrodes are utilized. Third, the response time is short enough to attain a steady potential, and also the drift is very small. Fourth, the large surface area of the platinum particles makes it possible to use the tubular hydrogen electrode both as a reference electrode and as a counter electrode at the same time. A practical reference electrode was proposed where the hydrogen evolution electrode by forced current from the outer circuit is made the reference electrode.[9] But the shift of potential from RHE was inevitable depending on the solution composition.

When there are cations other than H$^+$ in the solution, this would cause a Donnan potential at the interface between the polymer electrolyte and the outside solution.[5] According to the estimation, the deviation of the indication potential due to the Donnan potential E_{Don} when there are H$^+$ and Na$^+$ is expressed as follows[10]

$$E_{Don} = - \frac{RT}{F} \ln \left(\frac{\gamma_+ c_+(m)}{k_+ c_+(s)} \right) \qquad [5]$$

where γ_+ is the activity coefficient of the cation (H$^+$ or Na$^+$) in the membrane, and k_+ is the hypothetical partition coefficient of cation between solution and membrane phases, in the absence of sulfonic acid groups. Equating E_{Don} for H$^+$ and Na$^+$, one obtains

$$E_{Don} = - \frac{RT}{F} \ln \left(\frac{c_{SO_3^-}(m)}{2c_{SO_4^{2-}}(s)} \frac{1 + r_c}{\frac{k_H}{\gamma_H} + \frac{k_{Na}}{\gamma_{Na}} r_c} \right) \qquad [6]$$

When there is no Na$^+$, Eq. 6 becomes

Figure 11. Indication potential of tubular hydrogen electrode *vs.* SHE.

$$E_{\text{Don}}(\text{H}^+) = -\frac{RT}{F} \ln \left(\frac{c_{\text{SO}_3^-}(m) \, \gamma_\text{H}}{2c_{\text{SO}_4^{2-}}(s) \, k_\text{H}} \right) \qquad [7]$$

Here $c_{\text{SO}_3^-}(m)$ is the concentration of sulfonic acid groups in the membrane, $c_{\text{SO}_4^{2-}}(s)$ is that of SO_4^- (analytical) in the solution, and r_c is the ratio $c_{\text{Na}^+}(s)/c_{\text{H}^+}(s)$. Equation 7 is the same as the junction potential as shown in Eq. 3. The deviation of the Donnan potential due to the presence of Na^+ is written as follows

$$\Delta E_{\text{Don}} \equiv E_{\text{Don}} - E_{\text{Don}}(\text{H}^+) = -\frac{RT}{F} \ln \left(\frac{1 + r_c}{1 + \frac{\gamma_\text{H}}{\gamma_\text{Na}} \frac{k_\text{Na}}{k_\text{H}} r_c} \right) \qquad [8]$$

The value of $(\gamma_\text{H}/\gamma_\text{Na})(k_\text{Na}/k_\text{H})$ is estimated as 1.18 from the literature value of K_H^Na.[11] Suppose that $r_c = 1$, and Eq. 8 gives $\Delta E_{\text{Don}} = 2.2$ mV at 25°C and 2.6 mV at 80°C. Even in the case $r_c = 10,000$, Eq. 8 gives $\Delta E_{\text{Don}} = 4.3$ mV at 25°C and 5.0 mV at 80°C. This result means that the deviation becomes larger than several mV only when the Na^+ concentration in the solution reaches 10,000 times that of H^+ in the solution. For other cations, details are given in the Appendix.

When there is very little H^+ in the solution, the higher the tendency for the cation to exchange with H^+ in the polymer electrolyte, the larger the error would be in the measured potential. This is a disadvantage of the present electrode, and precautions must be addressed when the electrochemical system deviates from an acidic environment. But as long as the electrochemical measurements are conducted in solutions of fixed composition, the tubular hydrogen electrode can still be used as a reference electrode.

The temperature affects the potential of the tubular hydrogen electrode in two ways. First, the dependence through the Nernst equation causes a several millivolt positive shift when it is used at 70-80°C, but this can be corrected through a Nernstian fit. The second and the large factor in potential shift is due to the polymer swelling, which may shift the potential to the negative direction by an activity change of H^+ in the polymer. All these effects should be corrected by preparing calibration curves before the electrochemical measurements.

One of the promising features of the tubular hydrogen electrode is the application in fuel cell testing.[12] This is made possible due to its gastight structure, miniaturized size, and capability of sticking to small portions of the measuring system. An effective application of the tubular hydrogen electrode may be in fuel cell stacks. It is desired for the optimal design of fuel cell stacks to obtain knowledge about the potential distribution within a stack during the operation test. However, it is difficult to install reference electrodes in each of the cells comprising a fuel cell stack. Tubular hydrogen electrodes may fit into the cells to measure anode/cathode potentials by con-
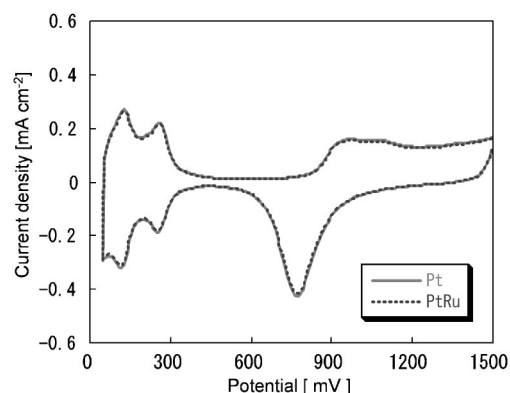
Table A-I. Estimated shift of Donnan potential ΔE_{Don} from H_2SO_4 system to $\text{H}_2\text{SO}_4 + \text{M}_2\text{SO}_4$ system.

M	K_H^M	r_c	ΔE_{Don}(mV)		
			25°C	40°C	80°C
Li	0.586	1	−6.0	−6.3	−7.1
		10	−12.1	−12.7	−14.4
		1000	−13.7	−14.4	−16.2
Na	1.18	1	2.2	2.3	2.6
		10	3.9	4.1	4.6
		1000	4.2	4.5	5.0
K	3.84	1	20.7	21.8	24.5
		10	30.3	31.8	35.9
		1000	32.0	33.6	37.9

tacting any components when they are necessary. In this case, the electrolyte membrane of each cell must be exposed outside to contact the tubular hydrogen electrode.

Conclusions

In this work, a new microtubular hydrogen electrode has been developed and evaluated as a reference electrode. Tubular hydrogen electrodes are easy to use as reference electrodes in both acid solutions and PEFCs. The advantage of tubular hydrogen electrodes over conventional glass body hydrogen electrodes are that they (*i*) have very small size with reversible and stable potential, (*ii*) are nonpolarizable and have no hysteresis, (*iii*) work as RHE for different pH electrolyte solutions, and (*iv*) are usable for two-electrode cells. However, tubular hydrogen electrodes cannot be used in electrolyte solutions containing cations other than H^+ like neutral or alkaline solutions. Tubular hydrogen electrodes require attention for the potential shift that occurs with temperature change. In fundamental studies, newly developed hydrogen electrodes are to be applied to evaluate diffusion rates of metal ions in polymer electrolyte membranes and also to elucidate phenomena at liquid junction interfaces.

Acknowledgment

Appendix

Supporting information on the microtubular hydrogen electrode developed for microanalytical and electrochemical purposes is described here. The fabrication of the Pt layer is done here by the chemical plating method with successful results. The Donnan potential corrections for H^+ and alkaline cation systems are discussed. Details of application of the microtubular hydrogen electrode to the fuel cell system are presented.
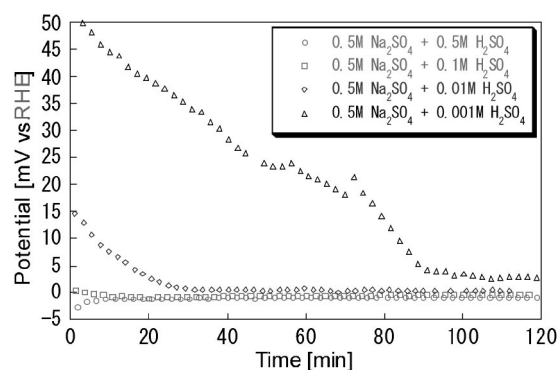

Figure A-1. CVs of Pt plate using tubular hydrogen electrode with Pt and PtRu plating in 1 M H_2SO_4 at room temperature. Sweep rate: 100 mV s^{-1}.

Figure A-2. Indication potential of tubular hydrogen electrode in mixture of H_2SO_4 and Na_2SO_4.
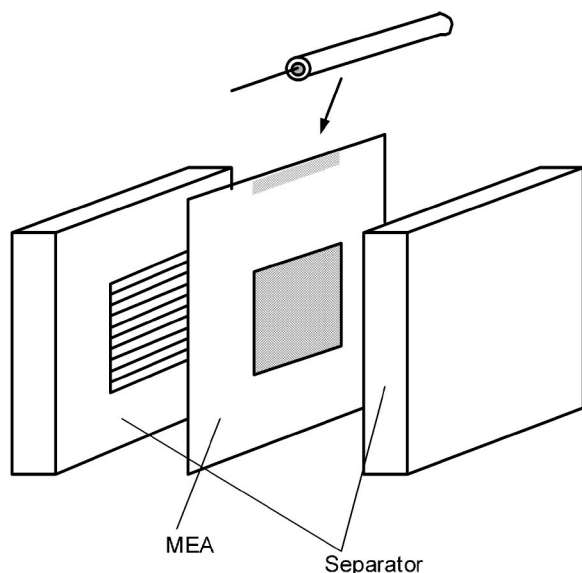
Figure A-3. Schematic picture of PEFC single cell with a tubular hydrogen electrode.

Figure A-4. Indication potential of tubular hydrogen electrode in PEFC.

Preparation of Pt or PtRu by chemical plating method.—— For the chemical plating method (impregnation-reduction method), tetraammineplatinum(II) chloride ([Pt(NH₃)₄]Cl₂) and pentaamminechlororuthenium(III) chloride ([RuCl(NH₃)₅]Cl₂), both from Wako Pure Chemical Industries, Ltd., were used as precursors for Pt and Ru, respectively. Cation exchange was carried out by immersing the tubular electrolyte membrane into a Pt complex solution or a mixture of Pt and Ru complex solutions (Pt:Ru atom % = 1:1) at room temperature. Subsequently, an NaBH₄ (90%, Wako Pure Chemical Industries Ltd.) alkali solution was injected inside the Flemion tube at 323 K to precipitate the Pt or PtRu layers. Residual precursors were removed by dipping in 1 M H₂SO₄ and DI water at 353 K.

The hydrogen electrode was made by injecting the mixing paste of carbon powder (Vulcan XC-72R, Cabot) and 5 wt % Nafion solution (Aldrich Chemical Company, Inc.) into the Pt or PtRu deposited tubular electrolyte containing a current-conducting Pt wire (Φ 0.1 × 50 mm, Nilaco Corp.).

Figure A-1 shows CVs of the Pt plate electrode measured using tubular hydrogen reference electrodes with Pt and Pt/Ru plating layers inside the tube. Both Pt and Pt/Ru mixed catalyst layers worked perfectly as reference electrodes in 1 mol/L sulfuric acid solutions. The indication potential was within ±0.5 mV in reference to RHE in 0.5 mol/L to 1 mol/L sulfuric acid solutions, respectively.

Donnan potential correction for H⁺ *and alkaline cation systems.*—— Equation 8 can be rewritten as follows, using the selectivity coefficients K_H^M

$$\Delta E_{Don} \equiv E_{Don} - E_{Don}(H^+) = -\frac{RT}{F} \ln\left(\frac{1 + r_c}{1 + K_H^M r_c}\right) \qquad [A-1]$$

The shift of the Donnan potentials from the pure H₂SO₄ system to H₂SO₄ + M₂SO₄ system (M = Li, Na, K) is estimated using Eq. A-1, with the assumption that the selec-

tivity coefficients in Ref. 11 do not change with temperature. Estimated ΔE_{Don} values are shown in Table A-I as a function of the ratio $r_c \equiv c_{M^+}/c_{H^+}$ and temperature. From the table, it is recommended that as the supporting electrolyte in the acid solution, Na⁺ solution should be used to minimize the Donnan potential shift, because for other systems using, *e.g.*, Li⁺ and K⁺, the shift becomes substantially large. Experimental results with H₂SO₄ + Na₂SO₄ system are shown in Fig. A-2, which indicates that as far as the solution is acidic, Na⁺ with large amounts does not interfere much with the indication potential.
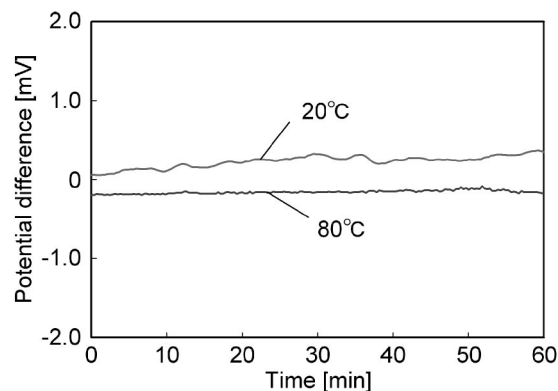
Application of tubular hydrogen electrodes to PEFC measurement.—— Tubular hydrogen electrode was glued to the membrane of a membrane electrode assembly (MEA) of a PEFC as shown in Fig. A-3, using 5 wt % Nafion solution (Aldrich). Humidified H₂ gas produced by bubbling it through a water pot was fed into the tube. When H₂ gas was supplied to the anode or the cathode of the PEFC, the potential stayed within 0.2 mV in reference to the tubular hydrogen electrode in a temperature range between 20 and 80°C, as shown in Fig. A-4.

References

1. J. Koryta, J. Dvořák, and L. Kavan, *Principles of Electrochemistry*, Chap. 3, John Wiley & Sons, Chichester (1993).
2. J. S. Newman, *Electrochemical Systems*, Chap. 5, Prentice-Hall, Englewood Cliffs, NJ (1973).
3. C. H. Hamann and W. Vielstich, *Elektrochemie I*, Chap. 4, VCH Verlagsgesell-schaft, Weinheim (1985).
4. *The Encyclopedia of Electrochemistry*, C. A. Hampel, Editor, p. 1010, Robert E. Krieger, Huntington, New York (1972).
5. K. J. Laidler and J. H. Meiser, *Physical Chemistry*, Chap. 8, The Benjamin/ Cummings Pub. Co., Menlo Park, CA (1982).
6. M. Kunimatsu and T. Okada, *Electrochem. Solid-State Lett.*, **7**, A389 (2004).
7. H. Qiao, M. Kunimatsu, and T. Okada, *J. Power Sources* **139**, 30 (2005).
8. W. E. Morf, *The Principles of Ion-selective Electrodes and of Membrane Trans-port*, Chap. 4, 5, Elsevier Scientific Publishing, Amsterdam (1981).
9. J. Giner, *J. Electrochem. Soc.*, **111**, 376 (1964).
10. K. Vetter, *J. Electrochemical Kinetics*, Chap. 1, Academic Press, New York (1967).
11. A. Steck and H. Yeager, *Anal. Chem.*, **52**, 1215 (1980).
12. W. He and T. V. Nguyen, *J. Electrochem. Soc.*, **151**, A185 (2004).