



Application of a hydrogen reference electrode to a solid state water removal device

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Abstract

An electrolytic water removal device using a solid polymer electrolyte membrane has been developed for controlling the humidity in the atmosphere of electrical control boxes. The device consists of a solid polymer electrolyte and thin film electrodes. The anode side of the device shows a dehumidifying effect while the cathode side shows a humidifying effect. This paper reports the evaluation and separation of the anode and cathode potentials by installing a gas port as a reversible hydrogen reference electrode attached to the water removal device. The polarization curves show that the anode potential remained stable at 2 V vs RHE, while the cathode potential changed significantly.

1. Introduction

An electrolytic water removal device using a solid polymer electrolyte membrane cell has been developed as a protective measure against problems caused by high humidity and to maintain high reliability by controlling the humidity in the atmosphere of electrical or power equipment. The device consists of a solid polymer electrolyte and thin film electrodes. The anode side of the cell shows a dehumidifying effect and the cathode side a humidifying effect [1, 2]. In this work, the potentials of each electrode were examined using a reversible hydrogen reference electrode (RHE). The water removal reactions involve the high overvoltage reactions of O₂ generation at the anode (dehumidifying) side and O₂ reduction at the cathode (humidifying) side. It is necessary to evaluate the anode and cathode potentials in order to improve the water removal efficiency. Gaseous reference electrodes such as RHE are more desirable than the aqueous reference electrodes such as saturated calomel electrode (SCE). Because in the SCE, the electrolytic solution (KCl aqueous solution) comes in contact with the solid polymer electrolyte membrane. In this case, there is a possibility of a large ionic conduction resistance change because water is supplied to the solid polymer electrolyte membrane by the electrolytic solution. On the other hand, because the RHE does not use an electrolytic solution but uses hydrogen and directly contacts with the solid polymer electrolyte membrane, the amount of water in the solid polymer electrolyte membrane may not be changed, and the ionic conduction resistance of the solid polymer electrolyte membrane may not be increased by the cation.

However, supplying pure hydrogen continuously to the reference electrode is difficult and inadequate from the standpoint of safety. Hence, we proposed a method of injecting about 10 ml of hydrogen to the electrode to serve as an RHE. In this method, hydrogen is intermittently supplied to the reference electrode gas port using an injector to measure the anode and cathode potentials. Using this method, one can conveniently make a polarization measurement in a field test of the water removal device, which is often installed in outdoor equipment. This paper reports the evaluation of the stability of the RHE of the water removal device and the evaluation of the anode and cathode potentials.

As another purpose of this report, the effect on the electrode potential when water was splashed onto the cathode was evaluated. The electric current is known to increase if water is added to the electrode by rainwater etc., and the occurrence of hydrogen takes place on the cathode. Though hydrogen is evolved not on the dehumidifying room side but on the outdoor side, it is preferable to prevent contact with water to assure safety. An attempt was made to elucidate the mechanism by which hydrogen forms, by examining the effect on the anodic potential and the cathodic potential with the RHE when water is added to the electrode.

2. Experimental method

The water removal device was prepared by hot-pressing a Pt-plated stainless steel web on both sides of a solid polymer electrolytic film; Nafion[®] 117 (Dupont Co.) The reference electrode was made of a Pt-plated stainless

steel web of diameter 5 mm hot-pressed on the centre of the cathode side of the solid polymer electrolyte of 10 mm diameter, separated from the cathode electrode area so as not to come into contact with the cathode. The reference electrode gas port, made of transparent acrylic resin (cylindrical form), was attached to the solid polymer electrolyte area using an adhesive. Through a hole on the gas port, H₂ gas was fed to the reference electrode using an injector. After injecting H₂ into the gas port, the hole was closed by tape (Scotch tape). The surface area of the electrode of the water removal device was 100 cm² for the anodic side, and 99 cm² for the cathode side. In the centre of the cathode a round hole of 10 mm was made, and the RHE electrode (surface area of the electrode: 0.2 cm²) was installed there. (The surface area of the cathode was less than that of the anode due to the surface area of the reference electrode) A stainless steel box of 30 cm × 30 cm × 60 cm size was used for the evaluation of the water removal effect. The stainless steel box was placed in the laboratory at 20 °C, 60% humidity, and oxygen concentration of 21%. The cathode side was exposed to the laboratory atmosphere: 20 °C temperature, 60% humidity, oxygen concentration of 21%, and they were almost kept constant.

The membrane resistance was measured by means of a milliohm meter (made by Matsushita Tsushin Co.) using the a.c. four-terminal method [3]. Figure 1 shows the model side view of the water removal device with a reference electrode. The water removal effect was measured by applying 3 V d.c. (Kikusui Co., model 101) between the anode and cathode electrodes. The temperature and humidity inside and outside the box were detected by a temperature and humidity sensor (Yamato Science Co., model YH 22S).

3. Experimental results

3.1. Water removal effect

Figure 2 shows the water removal effect of the device. The humidity in the box declined rapidly immediately

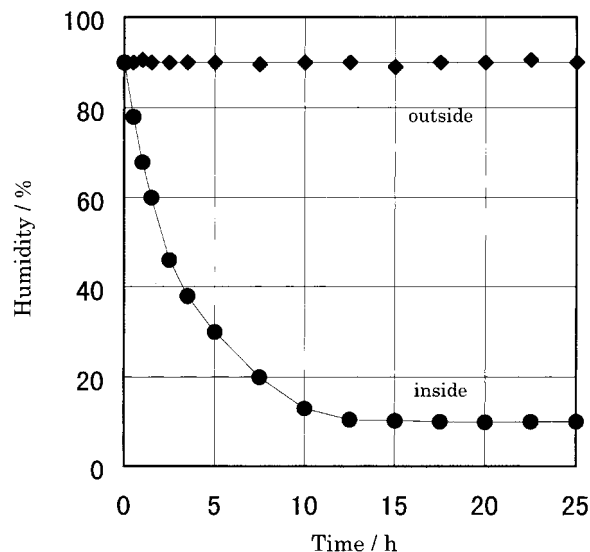


Fig. 2. Water removal effect.

after switching the power source on, then approached a steady level.

3.2. Evaluation of reference electrode (RHE) stability

The change in anode potential was examined by injecting 10 ml of pure H₂ into the reference electrode gas port. Here, the dehumidification chamber temperature (21 °C), humidity (57%), O₂ concentration (21%), applied voltage (3 V) and current (0.3 A), were all kept constant throughout the experiment.

Figure 3 shows the anode potential change with time, with the abscissa (horizontal axis) indicating the elapsed time account the H₂ injection time to be at 0 min. H₂ was injected twice every 30 min (injection times are indicated by an upward arrow marked ↑ in the Figure). The anode potential immediately after H₂ injection showed a sharp rise and reached a level of 1.9 V vs RHE, then the potential remained steady for about 4 min before falling gradually, showing an excessive fall after 13 min. When H₂ was injected again, the potential returned to the normal level 1.9 V vs RHE. From the

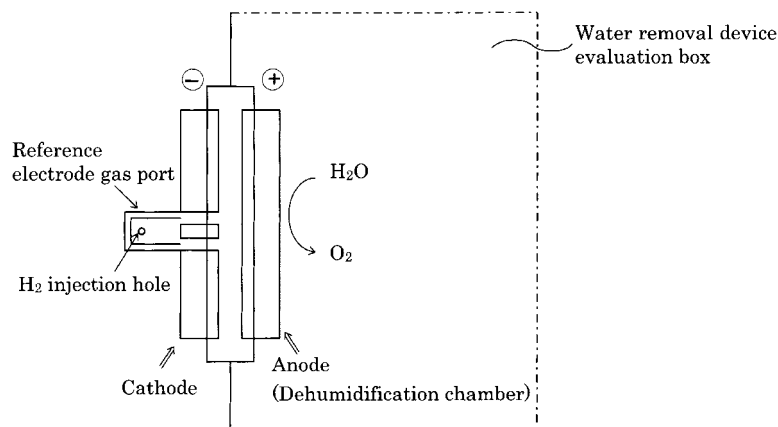


Fig. 1. Model diagram of the side (section) of the water removal device with a reference electrode.

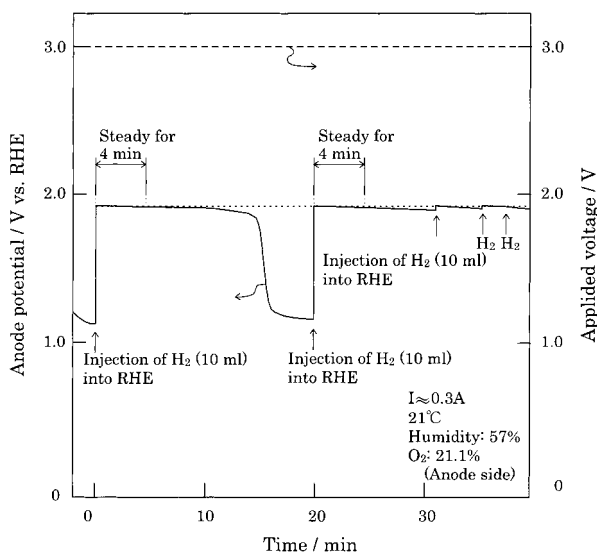


Fig. 3. Stability test of the hydrogen reference electrode (RHE).

above results, it could be assumed that the injected H_2 was consumed or diffused and dispersed, causing the H_2 concentration in the reference electrode gas port to decrease and to deviate from the RHE potential. These results show that the reference electrode can be used as an RHE by injecting H_2 into the reference electrode gas port at a time interval of 4 min.

3.3. Evaluation of current–potential characteristics

Having found that the RHE potential remains steady on injecting H_2 every 4 min, we measured the cathode potential (atmosphere side) and anode potential (dehumidification side) against the RHE by varying the applied voltage while injecting 10 ml H_2 using an injector at an interval of 4 min. The results are given in Figure 4. The broken line indicates the ohmic loss (iR) estimated from the current on the basis of the resistance ($R = 245 \text{ m}\Omega$: milliohm meter, AC 4-terminal method) when the voltage was not applied. When voltage was applied, the correct resistance could not be measured with a milliohm meter because of the internal resistance on the power source side associated with the measured resistance.

In Figure 4, the current shows a change (i.e., decreased) when the applied voltage indicated by open circle (ordinate, left side) reached a level of 3.5 ~ 4.5 V, which was probably attributed to the increase in internal resistance due to the change in the water content of the solid polymer electrolyte film as the dehumidification proceeds. The filled circle designates the anode potential and the filled delta the cathode potential (both given on the ordinate, right side). The cathode potential shows a great change from 0 V vs RHE, while the anode voltage remained stable at 2 V vs RHE or so, indicating that the cathode potential (atmosphere side) become largely changed when voltage was applied. The cathode potential seems to be in a diffusion-controlled stage by about 1 A.

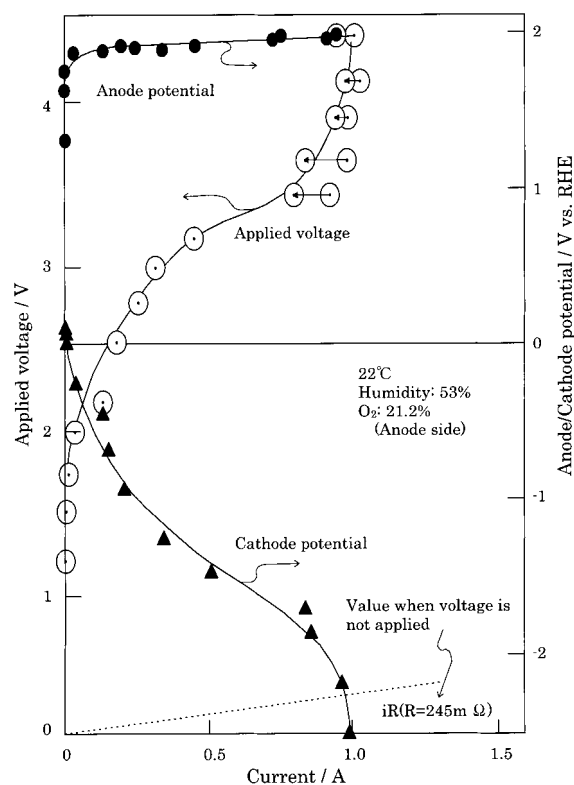


Fig. 4. I/V and change in anode/cathode potential.

From the above results, the anode potential was found to undergo less change and to remain stable at 2 V vs RHE, while the cathode potential showed a big change.

3.4. Effect of water addition to the cathode on potential curves (at constant voltage)

The change in current was examined by adding water (approximately 0.1 ml) to the stainless web of the cathode using an injector and maintaining the applied voltage constant at 2.5 V. Figure 5 shows the change in current (solid line; ordinate (vertical axis) on the left) and anode potential (broken line; ordinate on the right) after adding water for the first time. Water was added three times over 0 ~ 30 min. The current increased sharply immediately after the addition of water and attained peak levels before decreasing. The peak current exceeded 2.2 A, about 10 times larger than the 0.2 A, the current before the addition of water. This phenomenon was reproduced each time the water was added, and the current showed a similar peak value.

The anode potential, showed a slight upward shift (high potential side) after the addition of water, but returned to the original value as the current decreased. The change in the anode overpotential during the upward shift was less than 0.1 V. The anode potential showed a sharp fall after 7 min, which was attributed to the change in RHE potential because of the delay in the timing of injecting H_2 into the reference electrode port. The potential returned to its normal value when H_2 was injected (after 8 min).

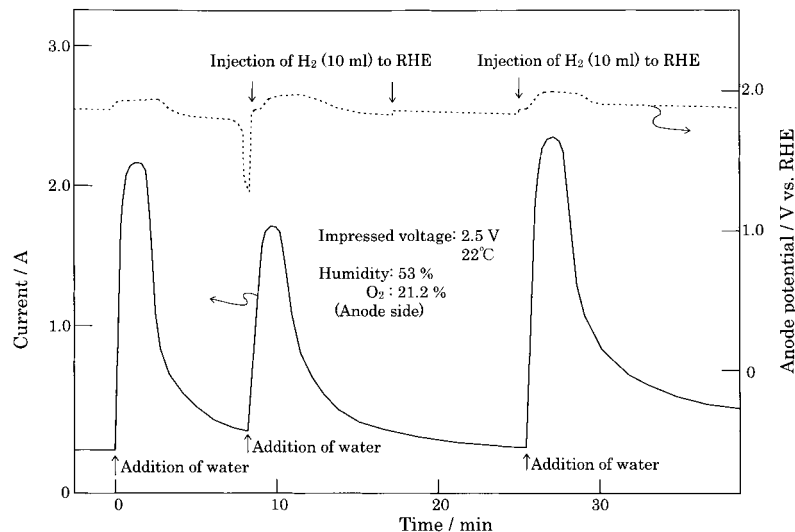


Fig. 5. Effect of water addition to the cathode side at constant voltage condition.

From the above results, the current temporarily increased 10 fold when water was added, while the anode potential during that time shifted by about 0.05 ~ 0.1 V.

3.5. Effect of water addition to the cathode (at constant current)

The change in applied voltage and cathode potential under constant current conditions was examined by adding water while maintaining the current constant at 0.5 A. Figure 6 shows the change in applied voltage (broken line; ordinate on the right) and cathode potential (solid line; ordinate on the left) with time, after adding 0.5 ml water. The applied voltage shows a sharp fall, from 3.5 V to 2.1 ~ 2.2 V, immediately after the addition of water while the cathode potential shows a large upward shift. The applied voltage and cathode

potential show a symmetrical change, with the variation in applied voltage with time largely depending on the change in cathode potential. This shows that the change in anode potential was small.

Figure 7 shows the result when the quantity of added water was reduced, with the water quantity (feed rate) expressed in terms of the water droplets from the injector. As expected, the applied voltage and cathode potential show a symmetrical change, indicating that the addition of water causes the cathode polarization to drastically decrease. The fall in cathode potential observed at around 20 min is probably due to the delay in H₂ injection to the gas port. Furthermore, small bubbles actively formed at the cathode side when water was added were confirmed to be H₂ gas. From the above results at constant current mode, it has been found that the applied voltage drastically decreases upon water addition; the change in applied voltage almost correlates

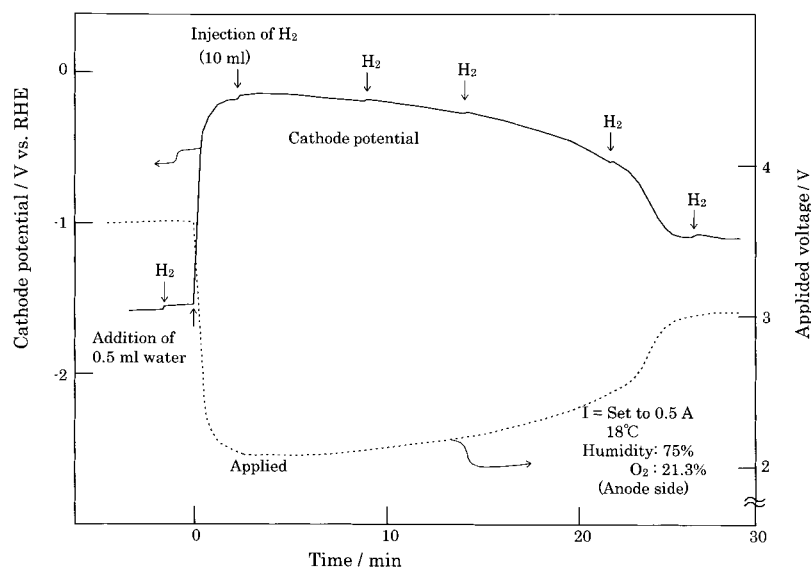


Fig. 6. Effect of water addition to the cathode side at constant current condition.

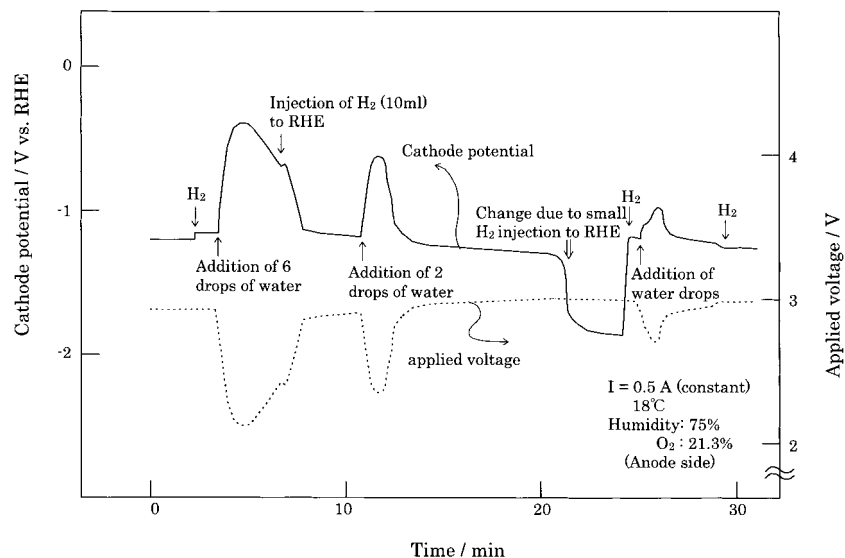


Fig. 7. Effect of water addition to the cathode side at constant current condition.

with the change in cathode potential, and H_2 gas is actively generated at the cathode.

4. Discussion

4.1. Reliability of reference electrode

We were able to evaluate the anodic potential and cathodic potential separately by installing an isolated electrode on a part of the cathode and injecting a small amount of hydrogen with a syringe by installing a reference electrode port when measurement was required. The potential could be stably measured for four minutes using 10 ml of hydrogen. Consequently, if a small amount of hydrogen gas is used, the performance of the water removal device can be conveniently evaluated, even outdoors.

The reliability of the reference electrode depends on the H_2 pressure in the reference electrode port. However, the deviation from the normal potential is expressed in terms of H_2 pressure, by the equation:

$$\begin{aligned} \Delta V &= \left(\frac{RT}{2F}\right) \Delta \ln P = \left(\frac{RT}{2F}\right) \times 2.303 \Delta \log P \\ &= -23 \text{ mV (decade)}^{-1} (25^\circ \text{C}) \end{aligned} \quad (1)$$

where P is H_2 pressure in the reference electrode in Pa and voltage deviation is in mV.

The voltage deviation from the RHE potential attains a value of 23 mV when the H_2 pressure decreases from 10^5 to 10^4 Pa, and 46 mV when the H_2 concentration decreases from 10^5 to 10^3 Pa. The decrease in H_2 pressure is attributed to the electrochemical reaction with O_2 in the air, proton consumption at the cathode, and diffusion and dispersion of H_2 into the air from the gas port. Although (as can be seen in Figure 3) the anode potential decreased by 30 mV in 10 min after injecting

H_2 into the gas port, indicating the fall of H_2 pressure from 10^5 to 10^4 Pa, it was still possible to distinguish anodic polarization from cathodic polarization.

One of the authors of this report previously reported the inhomogeneous distribution of polarization in the horizontal plane of a phosphoric acid fuel cell (PAFC) using a single cell equipped with multiple RHEs located around the electrodes [3–9]. The inhomogeneous distribution of polarization in the horizontal plane was observed near the surroundings of the electrodes when significant change of current density occurred due to fuel starvation [3–7], CO poisoning [4, 8] or chemical poisoning [9]. Such a phenomenon also observed in the case of a polymer electrolyte fuel cell (PEFC) using a single cell equipped with eight RHEs located around the electrodes [10]. However, the reliability of the RHEs in the PEFC single cell was poor compared with the case of PAFC. This is probably because the ionic resistance between electrodes and RHEs significantly increase due to dry out of membrane around the electrodes. Accordingly, RHE was set at the center of electrode in this report.

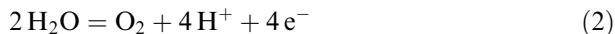
The milliohm meter is a handy measurement apparatus in which internal resistance is measured by the a.c. four-terminal method using the sine wave of 1 kHz. However, when a direct current power supply is used, it is difficult to measure the internal resistance because of too much noise when the electrical current flows even if the reference electrode is used. Consequently, measuring the internal resistance with the current interrupter method etc. is required, using a power supply with excellent response such as a potentiostat or a galvanostat [11].

However, this is not suitable for measurement in the case of a large electrical current and outdoor use. Another means is needed for the evaluation of the internal resistance when electrical current flows. Consequently, though the reference electrode used at this time

is handy, it has a disadvantage in that internal resistance is not evaluated for the measured anodic potential and cathodic potential.

4.2. Changes in anodic potential

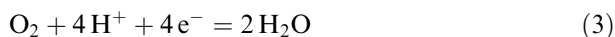
In the anode of the water removal device, oxygen and protons are formed by decomposing water in air. As a result, the humidity in the dehumidifying room decreases.



Reactions other than Equation 2 do not take place easily if the corrosion resistance of the anode is good. Reaction 2 takes place at a potential higher than 1.23 V vs RHE at normal temperature. In the experiment, the anodic potential was 1.8–1.9 V vs RHE and stable as shown in Figure 4. From this result, it is presumed that an overvoltage of about 0.6 ~ 0.7 V exists. In Figure 5, the anodic potential shifted to a noble potential by less than 0.1 V when water was added. This phenomenon is in contrast to the cathodic potential change by more than 1 V. Because the amount of the electrical current increased about 10 fold on adding water, the reason for the shift in anodic potential to a noble potential by 0.1 V can be attributed to the increasing overvoltage of the reaction. Even when the electrical current is increased 10 fold, the reaction at the anode is that of Equation 2. Though it is considered that the addition of water affects the change in the internal resistance of the solid polymer electrolyte membrane and the reaction of the cathode, the anodic potential did not change very much compared to the cathodic potential, in spite of the increase in electrical current about 10 fold.

4.3. Changes in cathodic potential

In the cathode of the water removal device, water is formed by the reaction of oxygen in air with a proton which has moved through the solid polymer electrolyte membrane and an electron which has passed through the external circuit. As a result, water is evolved to the atmosphere. Moreover, it is considered that a part of the water returns to the anode side through the solid polymer electrolyte membrane.



The reaction of Equation 3 takes place at a potential lower than 1.23 V vs RHE at room temperature. On the other hand, when the oxygen concentration in the cathode is insufficient, hydrogen is formed by a proton which has moved through the solid polymer electrolyte membrane and an electron which has passed through the external circuit.



Reaction 4 takes place stably at about 0 to -0.1 V vs RHE. However, hydrogen cannot be detected with a hydrogen detector on the cathode side in the usual conditioning of the water removal device; it is considered that hydrogen is not formed or is oxidized with oxygen to water even if hydrogen is formed. However, the formation of a large amount of hydrogen is observed not only with a hydrogen detector but also visually when water is added in this experiment. Consequently, it is considered that Reaction 3 is usually the main reaction, and when water is added, the reaction of Equation 4 becomes the main one. Figure 8 shows the potential chart when the applied voltage is 4 V based on the electrical current–potential characteristics of Figure 4. That with a high electronic level is the lower side. The entire ohmic drop is assumed to be caused by the internal resistance measured when the electrical current does not flow is applied to the cathode side for simplification. In Figure 8, it is assumed that Reaction 3 takes place at a potential lower than 1.23 V vs RHE and Reaction 4 at a potential lower than 0 V vs RHE. However, the cathodic potential is below -1 V in the potential chart when the applied voltage is 4 V, and this indicates the existence of an extremely large overvoltage. Moreover, because the cathodic potential was increased by 1 V or more when water was added, hydrogen was formed at a potential which was slightly lower than 0 V vs RHE. The formation of hydrogen at a potential which is slightly lower than 0 V vs RHE fits the theory. However, when water was not added, why was hydrogen not formed in spite of the potential being below -1 V? Two reasons for this phenomenon can be considered: (i) The oxygen reduction catalyst capability in the cathode is insufficient, and (ii) In the solid polymer electrolyte membrane near the cathode, the internal resistance rises, and the ionic conduction resistance of the solid polymer electrolyte membrane decreases rapidly on adding water.

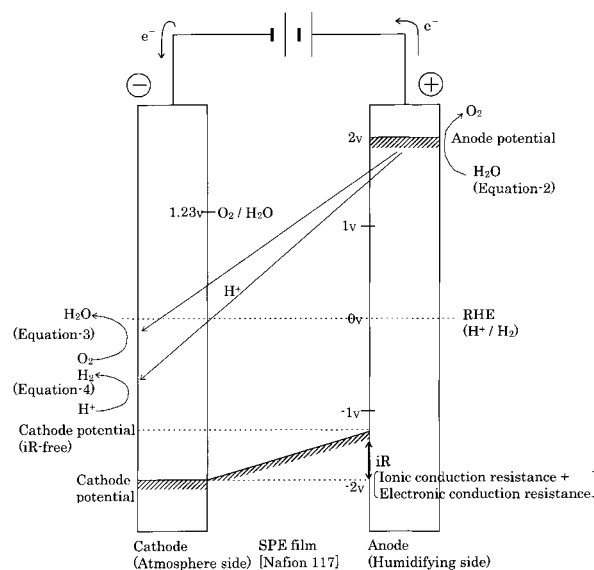


Fig. 8. Diagram related to potential of water removal device.

4.4. Changes in internal resistance

It is well-known that the ionic conduction resistance of a solid polymer electrolyte membrane changes greatly according to the amount of water included [12–14]. The ionic conduction in the solid polymer electrolyte membrane has been explained by the cluster model [15]. It is known that a proton moves in the solid polymer electrolyte membrane attended by several water molecules [16]. Water is always consumed by Reaction 2 on the anode, and water is carried to the cathode by movement of the proton. In Reaction 3 water is formed on the cathode. However, water is not formed on the cathode in Reaction 4. The amount of the water included in the solid polymer electrolyte membrane is greatly influenced by the electrical current. The consumed water increases as the electrical current increases. On the other hand, because the supply of water from air becomes a rate-determining step, it is expected that the water included in the solid polymer electrolyte membrane decreases extremely. Under such a condition, it is expected that the ionic conduction resistance increases according to the electrical current. In Figure 4, there is a possibility that the actual ionic conduction resistance increases exponentially compared with the ohmic drop (iR) value when the voltage is not applied. Although the amount of water included in the solid polymer electrolyte membrane is influenced by the temperature, because the amount of heat generated on the cathode where the overvoltage is large is more than that on the anode, there is a possibility that the temperature of the solid polymer electrolyte membrane in the cathode side increases, and the water included in it decreases locally. In addition, the internal resistance is possibly related to the position of the reference electrode. Because the distance between the RHE and anode is 0.2 mm or less, and the electrical current hardly flows to the RHE, it is presumed that the amount of water included in the solid polymer electrolyte membrane near the anode is sufficient. However, a distance of about 2 mm exists between the RHE and the cathode. There is a possibility that an insufficient amount of water is included in the solid polymer electrolyte membrane near the cathode. Further, when the water included in the solid polymer electrolyte membrane near the cathode decreases locally, the catalyst capability in the cathode is possibly also decreased by the decreasing reaction rate with the catalyst.

As mentioned above, some possibilities for the change in internal resistance causing a big change in the cathodic potential can be considered, and they should be clarified by examining the change in internal resistance under the condition of the electrical current flowing in the next step.

5. Conclusions

To evaluate the performance of the water removal device easily, also outdoors, a method of evaluating the

anodic potential and the cathodic potential by installing a simple model of an RHE, supplying hydrogen when needed, was developed. In conclusion, the following items were elucidated.

- (i) It is possible to operate a reference electrode as an RHE by injecting hydrogen intermittently with a syringe.
- (ii) When the applied voltage is increased, the cathodic potential changes greatly, and it shifts toward the base potential, though the change in anodic potential is small.
- (iii) When water is added, a large amount of hydrogen is formed, though it is hardly formed normally. When water is added at a fixed voltage, the electrical current increases 10 fold, and when water is added at a fixed electric current, the applied voltage decreases by about 1 V.
- (iv) When water is added, the anode potential shifts toward a noble potential by about 0.05 to 0.1 V, and the cathodic potential shifts to a noble potential by 1 V or more.
- (v) The amount of water included in the solid polymer electrolyte membrane and the ionic conduction resistance seem to be related to the change in the cathodic potential. The relation should be clarified by examining the changes in the internal resistance under the condition of the electrical current flowing in the next step.

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