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Effects of operating conditions on performance of high-temperature polymer electrolyte water
electrolyzer

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Abstract

Effects of operating conditions of a high-temperature polymer electrolyte water electrolyzer (HT-PEWE) on the electrolysis voltage are evaluated, and the optimal conditions for a high performance are revealed. A HT-PEWE unit cell with a 4-cm² electrode consisting of Nafion117-based catalyst-coated membrane with IrO₂ and Pt/C as the oxygen and hydrogen evolution catalysts is fabricated, and its electrolysis voltage and high-frequency resistance are assessed. The cell temperature and pressure are controlled at 80–130 °C and 0.1–0.5 MPa, respectively. It is observed that increasing the temperature at a constant pressure of 0.1 MPa does not increase the ohmic overvoltage of the cell; however, it does increase the concentration overvoltage. It is also found that the increase in the overvoltage resulting from the rise in the temperature can be suppressed by elevating the pressure. When operating the cell at a temperature of 100 °C, pressure greater than 0.1 MPa suppresses the overvoltage, and so does pressures greater than 0.3 MPa at 130°C. This behavior suggests that keeping the water in a liquid water phase by increasing the pressure is critical for operating PEWEs at high temperatures.

Keywords: High temperature, water phase, cell performance

1. Introduction

Global oil production is likely to reach its peak in the foreseeable future, and soon the world may suffer an oil shortage ^[1–3]. Therefore, renewable energy sources are attracting significant attention, as they may help

to solve pressing environmental and energy issues; and lead to a society where the renewable energy sources are the primary sources of electricity. However, the production of the renewable energy depends on time, and the sources are spread heterogeneously. This results in a mismatch between the energy supply and demand.

Hydrogen produced using a water electrolyzer powered by renewable energy ^[4] is an energy carrier that can help to overcome the supply-demand mismatch issue. Among the various types of electrolyzers being investigated, polymer electrolyte water electrolyzers (PEWEs) are probably good candidates for this role, as they can produce hydrogen at a low power consumption (e.g., 4.5 kW·h/(N·m³) at 80 °C and 0.3 MPa ^[5].

Although PEWEs have already been commercialized, further improvements in their performance are promising. In order to raise the performance of PEWEs, the catalyst layer must be improved. To achieve this goal, new catalyst structures and materials ^[6-8] have been proposed. In addition, attempts are being made to optimize the hydrophobicity and the pore size distribution of the current collectors ^[9-13]. Moreover, the impact of the flow behaviors of the vapor and liquid phases on the electrolysis performance is being investigated ^[14-16]. Simultaneously, some researchers pay attention on the electrochemical stability ^[17-23]. Furthermore, it has been proposed that increasing the operating temperature should improve the performance of PEWEs. Recent studies have suggested that the operating temperatures of 80–100°C increase the oxygen reaction rate ^[24] as well as the exchange current density ^[25], leading to a decrease in

the power consumption from 4.5 to 4.2 kW·h/(N·m³) at 100 °C and 0.3 MPa [5].

It has also been suggested that the polymer electrolyte membrane dehydrates during the high-temperature operation, reducing the ionic conductivity of the membrane as well as the performance of the PEWE [26]. Higher temperatures may increase the saturation pressure and reduce the relative humidity of the environment around the membrane, causing its water content and ionic conductivity to decrease. The dehydration of the membrane and the resulting decrease in performance have motivated researchers [5, 27–28] to develop composite membranes, based on the Nafion series of membranes with new catalyst structures. These composite membranes consist of a Nafion membrane, to which a hydrophilic material such as TiO₂ has been added. Composite membranes can maintain their ionic conductivity even at high temperatures, allowing PEWEs to exhibit higher performances than those operated at normal temperatures.

This study was also motivated by the aforementioned poor performance of PEWEs at high temperatures due to the dehydration of the membrane. Thereby, PEWE cell was electrochemically characterized under a wide range of temperature and pressure conditions. In conclusion, a strategy for improving the performance of PEWEs at high temperatures is suggested.

2. Experimental method

2.1 Functioning of a PEWE

(a). Piping and components.

(b). The flow field plate.

Fig. 1. Experimental setup used for evaluating the performance of a PEWE cell at high temperatures.

Figure 1 (a) shows the set up used to evaluate the performance of the PEWE cell. The piping for both the cathode and the anode passes through the cell, a pressure-reducing valve, a dehydrator, and a mass flow meter. A water pump is built into the anode piping. The hydrogen gas produced by electrolysis exits through the back pressure valve and water is removed from the gas at the dehydrator. The hydrogen and oxygen gases boost the pressure in the anode and cathode, respectively, while the back pressure valve controls the pressure. During water electrolysis, the ohmic resistance is measured using a high frequency resistance

(HFR) meter (Frequency: 10kHz; Model: 356E; TSURUGA ELECTRIC CORPORATION, JAPAN). The flow rates of the hydrogen and oxygen gases are also measured per second using a flow meter located in the downstream of the dehydrator in order to confirm the current efficiency. Due to the fluctuations,, the hydrogen and oxygen flow rates are determined by averaging the data populations recorded for 10 min.

Though the existence of preheater will be very helpful for controlling the water temperature at inlet and inside of the cell, de-ionized water was fed into cell directly without preheated. Specific points in our experiment may clarify this concern. Relatively small flow rates of water are chosen in our experiment. Under 1 A/cm² condition, the water utilization defined in dividing electrolyzed water by fed water is 2% and 20% for water feeding of 1.0 and 0.1 mL/min, respectively. This water utilization is much larger than that in conventional operation which is no more than 0.5% ^[17~20, 22~23], and suggests that water flow rate in our experiment is quite small. Moreover, the approach region running from cell inlet to flow channel is long, as shown in Fig. 1 (b). Taking into the consideration of small amount of water feeding, the long approach will give enough time to heat the fed water before the water reach the catalyst region, so that the temperature of fed water can be equilibrium to nominal temperature. The nominal temperature is obtained from thermocouple placed in flow field plate, whose temperature is stable in the experiment. These specific experimental conditions and cell configuration suggest that the nominal temperature is close to the temperature of water in the flow channel without preheating water at inlet.

2.2 Cell components

Table 1. Properties of the evaluated PEWE.

Component	Specification
Catalyst-coated membrane (CCM)	
Polymer electrolyte membrane (PEM)	Nafion117
Anode catalyst layer	IrO ₂ 1.5 mg/cm ²
Cathode catalyst layer	Pt/C 0.5 mg/cm ²
Electrode area	4 cm ²
Channel plate	
Anode material	Ti
Cathode material	Carbon
Channel width × height × length	1 mm × 1 mm × 33 mm
Pattern	Serpentine with 1 mm ribs
Current collectors	
Anode	Ti sintered compact with Pt plating Thickness: 0.3 mm Fiber diameter: 20 μm Porosity: 0.7 (400 g/m ²) Pt thickness: 1 μm (NIKKO TECHNO, JP.)
Cathode	SUS316L sintered compact Fiber diameter: 35 μm Porosity: 0.75 (600 g/m ²) Thickness: 0.3 mm (NIKKO TECHNO, JP.)
Flow field plate	
Anode/cathode	Titanium/carbon

A Nafion117membrane-based catalyst-coated membrane (CCM) was fabricated by spraying and hot pressing, as described in the following. As for the pretreatment, the Nafion membranes were treated in following processes: (1) The membrane is rinsed in the solutions composed of 5 wt. % H₂O₂ for 1 hour at 80°C, and (2) washed in de-ionized water for 1 hour at room temperature, and (3) rinsed in 8wt.% H₂SO₄

for 1 hour at 80°C, and finally (4) washed in de-ionized water for 1 hour at room temperature. Then, a slurry consisting of 67-wt% catalyst (IrO₂ powder, type IV, Tokuriki Co., Japan) and 33-wt% Nafion ionomer (5 wt% Ion Power solution) in deionized water and ethanol was prepared and sprayed onto one face of the membrane to form the anode catalyst layer. Commercial 46% Pt/C (Tanaka Kikinzoku Japan) powder was used as the catalyst for the cathode catalyst layer. In this case, a slurry was also prepared by mixing the Nafion ionomer and catalyst in water in a catalyst/dry ionomer weight ratio of 72:28. This slurry was sprayed onto the other face of the membrane to fabricate the cathode catalyst layer. The sprayed slurry was fixed onto the membrane by hot pressing. The loading rate of IrO₂ was 1.5 mg/cm², whereas that of Pt was 0.5 mg/cm². The area of the catalyst layers for the anode and the cathode was 4 cm².

The other components of the cell are listed in Table 1. An SUS316L mesh and a titanium mesh coated with platinum are used as the current collectors for the cathode and anode, respectively. Carbon and titanium plates were used as the cathode and anode flow field plates, respectively. Both flow field plates had serpentine channels. To form the PEWE cell, all the components were sandwiched between a pair of fastening plates and tightened them by 12 sets of bolt and nut at the torque of 4 Nm. This procedure and the area of flow field plate (64 cm²) make the tightening pressure to be about 3MPa.

2.3 Operating conditions

The PEWE cell was operated at temperatures of 80–130 °C and pressures of 0.1–0.5 MPa. Deionized water

at 20 °C was fed into the anode at flow rates of 0.1 mL/min and 1 mL/min; these flow rates correspond to the water utilization ratios (electrolyzed water/fed water) of 20% and 2%, respectively, for at 1 A/cm².

The water flow rates are lower than that used under normal operation for controlling the cell temperature and evaluating the performance of PEWEs at high temperatures. If the water flow rate was high, the cell temperature would either decrease or become unstable because of the sensible and latent heat of the fed water.

The characteristics of the probable flow pattern in the anode channel are listed in Table 2; the values were estimated based on the nominal temperatures and pressures between 80–130 °C and 0.1–0.5 MPa, respectively. The assumptions made for estimating the characteristics are as follows: (i) Faraday's electrolysis law is in effect; (ii) the current density is 0.5 A/cm² for determining the molar flow rate of oxygen gas, which is assumed to be an ideal gas; and (iii) the water in the channel could be described by the water phase equilibrium diagram at the nominal temperatures and pressures. With these considerations, the superficial velocities of the gas j_G (m/s) and liquid j_L (m/s) phases were computed. The comprehensive computation procedure is explained in the following.

Molar flux of produced oxygen gas and consumed water in anode channel is,

$$N_{O_2} = \frac{iA}{4F} \quad [1]$$

$$N_{cons} = \frac{iA}{2F} \quad [2]$$

Where, i is the current density, A is the active area of catalyst layer, F is the Faraday constant.

The molar flux of water vapor at outlet of anode channel is

$$N_{vapor} = \frac{N_{O_2} P_{sat}}{P - P_{sat}} \quad [3]$$

Where, P is the total pressure of gas in the flow channel, P_{sat} is the saturated pressure of vapor, and can be calculated as follow ^[29].

$$P_{sat} = -2846.4 + 411.24T - 10.554T^2 + 0.16636T^3 \quad [4]$$

Where, T is the operation temperature of cell, and its unit is °C.

If the $N_{vapor} + N_{cons} \leq N_{in}$, where N_{in} is the molar flux of liquid water at the inlet of anode channel, the molar flux of liquid water at the outlet in anode channel is,

$$N_L = N_{in} - N_{cons} - N_{vapor} \quad [5]$$

If the $N_{vapor} + N_{cons} \geq N_{in}$, all the liquid water is evaporated. Then,

$$N_{vapor} = N_{in} - N_{cons} \quad [6]$$

$$N_L = 0 \quad [7]$$

The volumetric flow rate of gas phase is,

$$V_G = \frac{(N_{vapor} + N_{O_2})R(T + 273)}{P} \quad [8]$$

Where, R is the molar gas constant. The volume velocity of liquid water in flow channel is,

$$V_L = \frac{N_L M_{H_2O}}{\rho_L} \quad [9]$$

Where, ρ_L is the density of liquid water, M_{H_2O} is the molar weight of water.

Thus, the superficial velocity of gas phase is,

$$j_G = \frac{V_G}{S} \quad [10]$$

Where, S is the area of cross section. The superficial velocity of liquid water.

$$j_L = \frac{V_L}{S} \quad [11]$$

Moreover, the pair of the superficial gas and liquid velocities at the nominal temperature and pressure is available to find the flow pattern via referring ^[30]. A two-phase flow is observed in the cases where the saturated pressure determined on the basis of the nominal temperature is lower than the nominal pressure. All two-phase flows can be categorized as slug flows. This is because the superficial velocities of gases are two to three orders of magnitude higher than the superficial velocities of liquids. On the other hand, a single-phase flow (e.g., a gas flow) is observed in the opposite case, that is, when the saturated pressure determined on the basis of the nominal temperature is higher than the nominal pressure.

Table 2 Values of the superficial gas velocity (j_G ; m/s), superficial liquid velocity (j_L m/s), and the ratio β ($= j_G / (j_G + j_L)$) at the outlet of anode flow channel. The characteristics of the flow pattern determined on the basis of these values are also shown.

(a) For a water flow rate of 0.1 mL/min.

	0.1MPa			0.2MPa			0.3MPa			0.5MPa		
	m/s	β	Pattern	m/s	β	Pattern	m/s	β	Pattern	m/s	β	Pattern
80°C	j_G 2.8*10 ⁻¹	0.995	2-Phases	9.8*10 ⁻²	0.985	2-Phases	5.9*10 ⁻²	0.976	2-Phases	3.3*10 ⁻²	0.957	2-Phases
	j_L 1.4*10 ⁻³		(slug)	1.5*10 ⁻³		(slug)	1.5*10 ⁻³		(slug)	1.5*10 ⁻³		(slug)
90°C	j_G 4.9*10 ⁻¹	0.997	2-Phases	1.2*10 ⁻¹	0.988	2-Phases	6.7*10 ⁻²	0.979	2-Phases	3.6*10 ⁻²	0.960	2-Phases
	j_L 1.3*10 ⁻³		(slug)	1.4*10 ⁻³		(slug)	1.5*10 ⁻³		(slug)	1.5*10 ⁻³		(slug)
100°C	j_G 2.7*10 ⁰	1	1-Phase	1.6*10 ⁻¹	0.991	2-Phases	7.9*10 ⁻²	0.982	2-Phases	4.0*10 ⁻²	0.964	2-Phases
	j_L 0		(gas)	1.4*10 ⁻³		(slug)	1.4*10 ⁻³		(slug)	1.5*10 ⁻³		(slug)
110°C	j_G 2.8*10 ⁰	1	1-Phase	2.7*10 ⁻¹	0.995	2-Phases	1.0*10 ⁻¹	0.986	2-Phases	4.5*10 ⁻²	0.969	2-Phases
	j_L 0		(gas)	1.3*10 ⁻³		(slug)	1.4*10 ⁻³		(slug)	1.4*10 ⁻³		(slug)
120°C	j_G 2.9*10 ⁰	1	1-Phase	1.5*10 ⁰	1	1-Phase	1.6*10 ⁻¹	0.992	2-Phases	5.5*10 ⁻²	0.975	2-Phases
	j_L 0		(gas)	0		(gas)	1.3*10 ⁻³		(slug)	1.4*10 ⁻³		(slug)

(b) For a water flow rate of 1.0 mL/min

	0.1MPa			0.2MPa			0.3MPa			0.5MPa		
	m/s	β	Pattern	m/s	β	Pattern	m/s	β	Pattern	m/s	β	Pattern
80°C	j_G 2.8*10 ⁻¹	0.945	2-Phases	9.8*10 ⁻²	0.856	2-Phases	5.9*10 ⁻²	0.783	2-Phases	3.3*10 ⁻²	0.667	2-Phases
	j_L 1.6*10 ⁻²		(slug)	1.7*10 ⁻²		(slug)	1.7*10 ⁻²		(slug)	1.7*10 ⁻²		(slug)
90°C	j_G 4.9*10 ⁻¹	0.968	2-Phases	1.2*10 ⁻¹	0.877	2-Phases	6.7*10 ⁻²	0.803	2-Phases	3.6*10 ⁻²	0.686	2-Phases
	j_L 1.6*10 ⁻²		(slug)	1.6*10 ⁻²		(slug)	1.7*10 ⁻²		(slug)	1.7*10 ⁻²		(slug)
100°C	j_G 1.7*10 ⁰	0.999	2-Phase	1.6*10 ⁻¹	0.906	2-Phases	7.9*10 ⁻²	0.828	2-Phases	4.0*10 ⁻²	0.707	2-Phases
	j_L 3.2*10 ⁻³		(slug)	1.6*10 ⁻²		(slug)	1.6*10 ⁻²		(slug)	1.7*10 ⁻²		(slug)
110°C	j_G 2.9*10 ⁰	1	1-Phase	2.7*10 ⁻¹	0.943	2-Phases	1.0*10 ⁻¹	0.861	2-Phases	4.5*10 ⁻²	0.733	2-Phases
	j_L 0		(gas)	1.6*10 ⁻²		(slug)	1.6*10 ⁻²		(slug)	1.6*10 ⁻²		(slug)
120°C	j_G 3.0*10 ⁰	1	1-Phase	2.6*10 ⁰	0.995	2-Phase	1.6*10 ⁻¹	0.906	2-Phases	5.5*10 ⁻²	0.769	2-Phases
	j_L 0		(gas)	1.4*10 ⁻²		(slug)	1.6*10 ⁻²		(slug)	1.6*10 ⁻²		(slug)

3. Results and discussion

3.1 Current–Voltage (I–V) characteristics

As stated previously, the PEWE operation at high temperatures causes the PEM to dehydrate and thus it increases the ionic resistance of the PEM. The degree of the dehydration is expected to rise when the water flow rate is low. Whether this is indeed the case was determined experimentally by increasing the operating temperature while keeping the flow rate low (0.1 mL/min) at 0.1 MPa.

Fig.2 Effect of temperature on the I–V performance for a water flow rate of 0.1 mL/min and pressure of 0.1 MPa.

Fig.3 Effect of temperature on the ohmic resistance for a water flow rate of 0.1 mL/min and pressure of 0.1 MPa.

The I–V characteristics of the cell at various operation temperatures are shown in Fig. 2. The rising temperature progressively decreases the open circuit voltage, confirming the thermodynamic expectations. The I–V characteristics in the low-current-density region were similar to those of a conventional PEWE. However, the I–V characteristics change in the high-current-density region. For instance, at 80 °C, the cell voltage started to increase sharply at 0.8 A/cm². With the elevation in the temperature, the point at which the sharp increase appears shifts towards the lower current-density region

Although the sharp increase in the voltage might suggests the dehydration of the PEM because of the high temperature and the low water flow rate, Fig. 3 shows contradicting results. The ohmic resistances for the different temperatures and current densities spread from 330 to 370 $\text{m}\Omega\text{cm}^2$, revealing a rise of 40

$\text{m}\Omega\text{cm}^2$ at most. This ohmic resistance rise corresponds to only a change of 20 mV in the cell voltage at 0.5 A/cm^2 . On the other hand, the sharp increase in the cell voltage is of the order of several hundreds of millivolts. Thus, changes in the ohmic resistance, which depends on the degree of dehydration of the PEM, do not explain the large increase in the cell voltage. The difference between the small ohmic voltage and the sharp voltage rise can be attributed to the concentration overvoltage. This attribution is justified in the following.

As the data at 0.1 MPa in Table 2(a) show, increasing the temperature converts the water phase from a binary (vapor/liquid) phase to a single vapor phase at around 100 °C. But the temperature is not the only factor which determines the water phase in flow channel. Current density also has an impact on the water phase change, because the more liquid water is consumed in the flow channel when current density become larger. Although the case of 80°C in table 2(a) suggests two-phase (liquid water remains), this holds under the current density of 0.5 A/cm^2 . Once the current density increases higher than 0.5 A/cm^2 , the two-phase turns to single phase. The temperature, at which the phase change occurs, decreases in the region of higher current density. Thus, table 2(a) with the impact of both current density and temperature on phase change is responsible for the unique I-V characteristic shown in Fig. 2.

3.2 Effect of water flow rate

The concentration overvoltage is ascribed to a shortage of the reactant water in the catalyst layer. An

increase in the water supply, i.e., a rise in the water flow rate is anticipated to decrease the concentration overvoltage.

Fig.4 Effect of the water feed flow rate on the I–V characteristics for a pressure of 0.1 MPa and temperature of 100 °C.

Fig. 4 shows the effect of the water flow rate on the I–V characteristics for the pressure (0.1 MPa) and temperature (100 °C) corresponding to the data in Fig. 2. In the whole range of the current density, the cell voltage for 1.0 mL/min is lower than those for 0.1 mL/min. It should be noted that, for a flow rate of 1.0 mL/min, there is no sharp increase in the cell voltage. Furthermore, the current density is higher in the case of 1.0 mL/min. Because the temperature and pressure corresponding to the flow rates of 1.0 and 0.1 mL/min were the same, it can be concluded that higher water flow rate diminishes the concentration overvoltage, and thus allowing for the higher current density operation.

A comparison of the data in Tables 2(a) and 2(b) confirms the conclusion drawn from the effect of the water flow rate. According to the data corresponding to 0.1 MPa and 100 °C, the flow patterns for 0.1 and 1.0 mL/min are single-phase vapor and two-phase vapor/liquid flows, respectively. Although the flow behavior in the catalyst layer at the anode is not known, the two-phase flow is expected to provide a higher amount of water being available at the catalyst layer. Thus, the higher flow rate of 1.0 mL/min reduces the concentration overvoltage and suppresses the sharp rise in the cell voltage.

Fig.5 Effect of the water flow rate on the ohmic resistance for a pressure of 0.1 MPa and temperature of 100 °C.

Fig. 5 presents the ohmic resistances for the flow rates of 1.0 and 0.1 mL/min. It is worth noting that the drop in the ohmic resistance of the cell by the increase in the water flow rate is so small that it does not impact the I–V characteristics. For example, the difference in the ohmic resistances for the two cases corresponding to 0.6 A/cm² is approximately 60 mΩcm²; this is equivalent to a difference of 36 mV in the

cell voltages. This difference is significantly smaller than the difference of 800 mV in electrolysis voltages observed in Fig. 4. Therefore, as mentioned above, the reason for the increase in the cell voltage in the case of 0.1 mL/min must be the concentration overvoltage, not the dehydration of the PEM.

In addition, Fig. 5 displays that the ohmic resistance decreases as the current density grows. As can be seen from the experimental setup in Fig. 1, no water is supplied to the cathode. This means that the PEM is supposed to become dehydrated, especially on the cathode side. On the other hand, the electro-osmosis transport of water is expected to hydrate the PEM on the cathode side when the electrolysis current is applied. This process, in which the electro-osmosis of water hydrates PEM, is thought to function in this experiment. As a result, the ohmic resistance decreases with an increase in the current density.

In summary, the aforementioned findings indicates that the overvoltage is mainly constituted by the concentration overvoltage. As proved in Fig. 4, the concentration overvoltage can be suppressed by increasing the water flow rate.

This result is here compared with some related study^[23], which also evaluated PEWE performance under vapor electrolysis condition (temperature of 130°C and pressure of 0.1MPa) and liquid water electrolysis condition (temperature of 80 °C and pressure of 0.1MPa), The study figured out that electrolyzing water at vapor phase performed worse due to a high IR overvoltage. Whereas, in our study, high concentration overvoltage caused by insufficient water supplement to catalyst layer is the main reason for high cell voltage in vapor electrolysis case. The difference between the two studies is considered to

attribute to different types of membranes used in present study and Xu et al.'s^[23]. Our study used Nafion 117, but Xu et al. used AquivionTM membrane in 80°C case and H₃PO₄ doped AquivionTM membrane in 130°C case. Generally, the properties of membrane has a large impact on both IR overvoltage and IR-free overvoltage^[5, 27]. Thus, the different membranes and their properties possibly cause the different result.

As mentioned in section 2.3, decreasing the water flow rate is the key to ensure the high-temperature operation of PEWEs. This is because the fed water, which is supposed to be at room temperature, cools the cell owing to its latent and sensible heats. The latent and sensible heat give rise to temperature fluctuations within the cell, making it difficult to maintain high temperatures. It is worth noting that increasing the water flow rate to levels higher than 1.0 mL/min did not decrease the cell voltage in other experiments. Thus, it can be concluded that the water flow rate of 1.0 mL/min, which corresponds to a water utilization rate of 2%, is the appropriate one for ensuring high-temperature PEWE cell operations while suppressing the concentration overvoltage.

3.3 Effect of pressure.

Fig.6 Effect of the pressure on the I–V characteristics for a water flow rate of 0.1 mL/min and temperature of 100 °C.

Fig.7 Effect of the pressure on the ohmic resistance for a water flow rate of 0.1 mL/min and temperature of 100 °C.

Higher pressures are also thought to be effective in reducing the concentration overvoltage. At a

certain temperature, an increasing pressure changes the water phase from vapor to liquid. As shown in Table 2(a), rising the pressure from 0.1 to 0.2 MPa at 100 °C converts the water phase from the vapor phase to the vapor/liquid phase (i.e., slug phase). Such a phase change is expected to increase the amount of water available at the anode catalyst layer, reducing the concentration overvoltage.

Fig. 6 illustrates the effect of the pressure on the I–V characteristics at a temperature of 100 °C and water flow rate of 0.1 mL/min. The pressure-rise means that the pressure at both the anode and the cathode elevates from 0.1 to 0.2 MPa. Although this rise in the pressure makes the open circuit voltage slightly higher, the sharp increase in the cell voltage disappears; and the current-density region becomes larger. Thus, rising the pressure is an effective method for transporting water in liquid phase from the channel to the catalyst layer in the anode, and thus suppressing the concentration overvoltage.

The pressure has also a positive influence on the ohmic resistance, as shown in Fig. 7. As is known, when the water around the PEM changes from vapor to liquid, the water content and hence the ionic conductivity in the PEM becomes higher ^[31]. Accordingly, the decreasing ohmic resistance with the increasing pressure is attributed to the rising water phase within the PEM.

3.4 Optimal operating conditions

(a) For a water flow rate of 0.1 mL/min.

(b) For a water flow rate of 1.0 mL/min.

Fig.8 Effects of the temperature and pressure on the cell voltage at 1 A/cm².

Fig. 8(a) shows the cell voltage for an electrolysis current of 1.0 A/cm² and water flow rate of 0.1 mL/min.

The data shown correspond to the cases when the cell voltage was lower than 3.0 V. The data in Table 2(a)

suggest that the flow pattern corresponding to the data plotted in Fig. 8(a) can be categorized as a two-phase flow; an exception is the case at 120 °C and 0.2 MPa. Although the data are scattered in Fig. 8(a), generally higher temperatures and pressures decrease the cell voltage, resulting in better cell performance. The impact of the temperature can be primarily attributed to the change in the activation overpotential.

As mentioned above, the change in the water phase from the single vapor phase to a vapor/liquid binary phase explains the impact of the temperature and pressure on the performance of PEWEs. Keeping water in the liquid phase can suppress the concentration overvoltage, as shown in Fig. 6. A change in the water phase occurs at the boiling temperature of water corresponding to the operating pressure. For instance, the water boiling temperatures corresponding to 0.1, 0.2, 0.3, and 0.5 MPa are 100 °C, 117 °C, and 133 °C, and 152 °C, respectively. This suggests that increasing the pressure from 0.1 to 0.2 MPa rises the maximum operating temperature from 100 to 117 °C. This is confirmed by the red line in Fig. 8(a); where the cell voltage at 0.2 MPa decreases monotonically as the operating temperature increases up to 117 °C. Once the temperature is greater than 117 °C, the water phase transforms from a vapor/liquid binary phase to the vapor phase. This phase transform results in a decrease in the amount of water available, thus and increase in the concentration overpotential, which appears as a sharp rise in the cell voltage. This argument, that the maximum operating temperature can be as high as the boiling temperature of water corresponding to the operating pressure can also be confirmed from the characteristics displayed for pressures of 0.3 and 0.5 MPa in Fig. 8(a).

The data in Table 2(a) gives a further discussion on how the temperature and pressure change the water phase and thus the cell voltage. For example, the water flows at 0.3 and 0.5 MPa are categorized as two-phase flows irrespective of the temperature. As long as the two phase flow is sustained, decreasing cell voltage with respect to the temperature appears at 0.3 and 0.5 MPa in Fig. 8(a). Consequently, increasing the pressure and maintaining a vapor/liquid two-phase flow are critical for the high-temperature operation of PEWEs, especially for high water utilization rates, which are ideal for controlling and stabilizing the cell temperature.

Figure 8(b) depicts the variation of the cell voltage against the temperature for diverse pressures for 1.0 mL/min. The results are generally similar to those observed for 0.1 mL/min, shown in Fig. 8(a). Namely, higher temperatures and pressures reduce the cell voltage. Moreover, a detailed comparison of these two flow rates indicates that, for a given operating pressure, the attainable temperature in the case of the low utilization rate (high flow rate) is greater than that in case of the high utilization rate. The comparison also suggests that the attainable temperature is greater than the boiling temperature of water. A low utilization rate seems to suppress the concentration overvoltage and hence enable PEWEs to operate at temperatures even higher than the water boiling temperature for a given operating pressure.

Although it is deduced that a large water flow rate is desirable for suppressing the concentration overvoltage, such a water flow, whose temperature might be equal to the room temperature or lower than the cell temperature, would decrease the cell temperature owing to the sensible and/or latent heat of water.

Therefore, an increase in the operating pressure for a given operating temperature appears to be a substantial factor to improve the performance of high-temperature PEWEs.

In this study, the whole experiment was completed with two sheets CCMs composed of Nafion117 membrane: one CCM was used in the experiment for 0.1mL/min case and the other was for 1mL/min case as shown in Fig.8. Both of the CCMs functioned over 80 hours in the high temperature condition above 100 °C. No fluctuation of cell voltage to a given condition was found during this period. Such result suggests that Nafion117 membrane is durable under the high temperature at least for dozens of hours. To clarify the durability of Nafion membrane quantitatively, future study is its high temperature life-cycle test comparing some other candidates of membrane, such as Aquivion membrane as expected in the use of high temperature operation.

4. Conclusions

A PEWE operating at a wide range of temperatures and pressures was electrochemically characterized for two different water flow rates. The water flow rate was relatively low, in comparison with that set in the normal operation. The analyses of the characterization results suggest the following conclusions:

1. The large overvoltage observed at elevated temperatures can be attributed to the water concentration overvoltage.
2. In addition to supplying a larger water flow rate, increasing the operating pressure also reduces the concentration overvoltage.

3. For suppressing the concentration overpotential, a vapor/liquid two-phase flow should be maintained through careful controlling the operating pressure and temperature. For instance, an operating pressure of 0.3 MPa corresponds to a boiling temperature of 133 °C; thus, the operating temperature can be increased to this level, causing the water in the cell to be in a vapor/liquid two-phase state.

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