Title

Optimum Structural Properties for an Anode Current Collector Used in a Polymer Electrolyte Membrane Water Electrolyzer Operated at the Boiling Point of Water

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Abstract

This study attempts to optimize the properties of the anode current collector of a polymer electrolyte membrane water electrolyzer at high temperatures, particularly at the boiling point of water. Different titanium meshes (4 commercial ones and 4 modified ones) with various properties are experimentally examined by operating a cell with each mesh under different conditions. The average pore diameter, thickness, and contact angle of the anode current collector are controlled in the ranges of 10–35 μm , 0.2–0.3 mm, and 0–120°, respectively. These results showed that increasing the temperature from the conventional temperature of 80°C to the boiling point could reduce both the open circuit voltage and the overvoltages to a large extent without notable dehydration of the membrane. These results also showed that decreasing the contact angle and the thickness suppresses the electrolysis overvoltage largely by decreasing the concentration overvoltage. The effect of the average pore diameter was not evident until the temperature reached the boiling point. Using operating conditions of 100°C and 2 A/cm², the electrolysis voltage is minimized to 1.69 V with a hydrophilic titanium mesh with an average pore diameter of 21 μm and a thickness of 0.2 mm.

Keywords

Current collector, Thickness, Contact angle, Pore diameter, Electrolysis voltage

Body

1 Introduction

The polymer electrolyte membrane water electrolyzer (PEMWE) has many advantages in hydrogen gas production because of its high operating current density, the high purity of the produced gas, and its compact structure. [1] A PEMWE consists of a catalyst coated membrane (CCM), current collectors, bipolar plates with flow channels, bus plates, manifolds, and end plates. The current collector is a porous medium placed between the CCM and the flow channel at both electrodes. The major functions of the current collector are (1) transferring the product and supplying the reactant effectively, (2) providing mechanical support for the membrane, and (3) collecting the current. Usually a titanium mesh is used as an anode current collector (ACC) due to the high overvoltage, the high oxygen concentration, and the severely acidic environment on the anode side. [2-4] Generally, a hydrophilic material is used in the ACC to attract reactant water from the flow channel to the catalyst layer and to remove the product oxygen from the catalyst layer to the flow channel simultaneously.

In recent years, many efforts to optimize the ACC structural properties have been made to manage the mass transfer through the ACC. Grigoriev et al. tested various optimizations of the ACC properties, and they suggested that the optimum average pore diameter of ACC is around 12 μm when the ACC thickness ranges from 0.8 to 1.4 mm. [5, 6] Hwang et. al and Ito et. al studied the effect of the titanium fiber diameter and the average pore diameter of the titanium mesh, finding that both the optimum fiber diameter and the optimum average pore diameter are around 20 μm when the ACC thickness is approximately 0.3 mm. [7, 8] Additional research suggests that the porosity should be in the range of 30-75% [7-10] because too low porosity hinders the transfer of gas while too

high porosity decreases the amount of water trapped in the hydrophilic ACC. [4] Ioroi et. al. and Hwang et. al. investigated the effect of wettability by adding TiO₂ powder and PTFE into the titanium mesh, finding that a hydrophilic ACC exhibits better performance than a hydrophobic one, but the exact value of contact angle in the wettability measurements is not given. [11,12]

While the properties of the ACC described above are significant, [4-12] the previous research has been conducted at temperatures such as 70°C and 80°C. Operating a PEMWE at a higher temperature is expected to improve its performance, but whether these optimized properties are maintained at a higher temperature remains unclear.

The costs and benefits of a PEMWE operating at high temperature are summarized as follows. An elevated temperature can (1) benefit heat recovery and thermal management, [13] (2) increase the efficiency of energy usage by accelerating the oxygen evolution reaction, [14-24] (3) reduce the amount of noble metal used and thus its cost, [16] and (4) allow for a compact structure for the PEMWE. [17] When the operating temperature increases beyond the boiling point of water, the two-phase flow in the cell will turn into a gas phase flow, which can easily be managed. [25] On the other hand, the cell performance will suffer from membrane dehydration and a high ohmic overvoltage. [20-24] Thus, to suppress the dehydration, the cell is pressurized to keep water in the liquid phase rather than in the gas phase. [20-24] However, the elevated pressure then requires a sealing material for the cell and a method to prevent gas leakage. [26]

To exploit the advantages of higher temperatures while avoiding membrane dehydration, we propose increasing the temperature up to the boiling point of water. When the temperature is near the boiling point, a disordered two-phase flow during the active phase change of water occurs [27-28] with the presence of liquid water expected to

hydrate the membrane and thus suppress the high ohmic overvoltage. [21-24] In addition, increasing the temperature up to the boiling point does not require additional pressurization to keep water in the liquid phase, and thus the development of sealing materials is unnecessary.

Therefore, we aim to clarify the following issues: (1) whether increasing the temperature to the boiling point of water can maintain the benefits of high temperatures without dehydrating the membrane, (2) whether the influence of the ACC on the performance of the cell at lower temperatures is maintained at the boiling point, and (3) how the ACC properties (thickness, water contact angle, and average pore diameter) affect the electrolysis cell performance.

2. Experiment

The experimental system for evaluating the electrolysis cell performance in this study consists of two vapor traps for separating hydrogen/oxygen from water, two mass flow meters for measuring the flow rate of the product gases, a water pump for introducing water into the anode, and two back pressure valves for controlling the pressure of anode and cathode. All the experiments are conducted at temperatures of 80°C and 100°C at a pressure of 0.1 MPa. The water is only introduced into the anode at a rate of 1 mL/min at room temperature, and water utilization is about 2% at 1 A/cm².

De-ionized water was introduced into the cell directly at room temperature because the flow rate of water was relatively slow (1 mL/min). At a current density of 1 A/cm², the water utilization is 2%, which is much larger than in typical electrolysis cells (around 0.5%) [29-35], suggesting a low flow rate. At the same time, the approach region running from the cell inlet to the flow channel is long, as shown in Fig. 1. This long approach and

the slow flow rate of water provides enough time to heat the introduced water to the nominal experimental temperature before the water reaches the catalyst layer. The nominal temperature was measured from a thermocouple placed in the flow field plate, whose temperature was stable in the experiment. These specific experimental conditions and the cell configuration suggest that the nominal temperature was close to the temperature of the water in the flow channel.

Fig. 1. Flow field plate used in this study.

The Nafion®-117-membrane-based CCMs were fabricated by spraying the catalyst onto the membrane followed by hot pressing. The Nafion® membranes were first pretreated using the following processes: (1) rinsing in an aqueous solution composed of 5 wt% H₂O₂ for 1 h at 80°C, (2) washing in de-ionized water for 1 h at room temperature, (3) rinsing in 8wt% H₂SO₄ for 1 h at 80°C, and finally (4) washing in de-ionized water for 1 h at room temperature. The resulting pretreated membranes were then sprayed with IrO₂ and Pt/C and pressed. The loading of IrO₂ (IrO₂ powder, type IV, Tokuriki CO.,

Japan) is 1.5 mg/cm² on the anode side, and the loading of Pt/C (46 wt.%, Tanaka Kikinzoku Kogyo, Japan) is 0.5 mg/cm² on the cathode side. The catalyst area for both the anode and the cathode is 4 cm².

Hydrophobic titanium powder with an average grain diameter of 20 µm (Toho Titanium, Japan) was used to change the hydrophobicity and pore size distribution. The series of treatments shown in Table 1 [36] were performed to control the wettability of the titanium powder.

Table 1. Treatments applied to the titanium meshes [36].

Procedure	Treatment
1	+ 200mg/cm ³ of Ti powder (average pore diameter is 20 µm)
2	+ 300mg/cm ³ of Ti powder (average pore diameter is 20 µm)
3	Washed by demineralized water for 1 min
4	Rinsed in NaOH solution (2 mol/L, 323K) for 1 min
5	Calcination at 450°C for 1 h

Four commercially available titanium meshes (Nikko Techno, Japan) and four modified ones were used for the ACC with the details shown in Table 2. CC1 to CC4 are the titanium meshes without any treatment that have different porosities and thicknesses. CC4-1 to CC4-4 are based on CC4 with controlled pore diameters and wettability. Carbon paper SGL34BA (CC6) and SUS316L mesh (CC5) are used for the cathode current collector. The pore diameters of the titanium meshes (CC1 to CC4 and CC4-3 to CC4-4) and the SUS316L mesh (CC5) were measured using the mercury penetration method. The pore diameter of carbon paper SGL34BA (CC6) was measured using the capillary flow porometry method. CC4-1, CC4-2 and CC4-3 share the same pore diameter distribution because the treatment to produce CC4-2 and CC4-3 has no impact on the pore diameter

distribution. The contact angles of all of the above current collectors were measured by the sessile drop method.

Table 2. Properties of the anode (CC1-CC4-4) and the cathode (CC5 and CC6) current collectors

Sample number	Mean pore diameter, μm	Contact angle, $^\circ$	Thickness, μm	Porosity, %	Treatment in Table 1	Matrix
CC1	34	0	300	70	Null	Titanium
CC2	20	0	300	60	Null	Titanium
CC3	35	0	200	70	Null	Titanium
CC4	21	0	200	60	Null	Titanium
CC4-1	14	120	200	54	CC4+1	Titanium
CC4-2	14	10	200	54	CC4+1+3+4	Titanium
CC4-3	14	0	200	54	CC4+1+3+4+5	Titanium
CC4-4	10	0	200	50	CC4+2+3+4+5	Titanium
CC5	60	15	300	75	Null	SUS316L
CC6	15	110	300	70	Null	Carbon

Carbon and titanium plates are used as the cathode and the anode flow field plates, respectively, each with serpentine channels. To form the PEMWE cell, all the components were sandwiched between a pair of fastening plates and tightened by 12 sets of nuts and bolts at a torque of 4 Nm. This procedure and the area of the flow field plate (64 cm^2) produce a tightening pressure of about 3MPa. The cell assembled with the above components was then mounted in the experimental system and operated to measure the current-electrolysis voltage (I-V) characteristics and the high frequency resistance (HFR). HFR was measured with a high frequency resistance meter (Frequency: 10kHz; Model: 356E; Tsuruga Electric CO., Japan) and is responsible for the ionic resistance through the PEM. The cell voltage was recorded at certain current densities in the range from 0.01 to 2.0 A/cm^2 . The average cell voltage over the 10 mins measurement time was recorded. This measurement was repeated three times, which shows that the current-voltage characteristics were reproducible and that the ACC was stable.

3 Results and discussion

3.1 The impact of the average pore diameter and thickness on the electrolysis cell performance at 80°C.

As a preliminary test, the effect of the ACC structural properties chosen in this study is examined at 80°C. The electrolysis cell performance is measured at 80°C and 0.1 MPa with different titanium meshes (CC1, CC2, CC3 and CC4 in Table 2). Fig. 2 (a) and 2(b) show the experimental I-V and I-HFR characteristics. CC1 and CC2 share the same thickness as do CC3 and CC4, while CC1 and CC3 have the same average pore diameters, as do CC2 and CC4. The electrolysis voltage difference between CC1 and CC2 or between CC3 and CC4 is less than 10 mV. In contrast, the electrolysis voltage difference between CC1 and CC3 or between CC2 and CC4 in Fig. 2(a) is clearly 100 mV, although the differences in HFR cannot explain this difference in the I-V characteristics.

The above experimental results at 80°C and 0.1 MPa imply that while the average pore diameter has little impact on the performance of an electrolysis cell in the range of 20 to 35 μm , the thickness has a clear impact on the electrolysis cell performance in the range from 0.2 to 0.3 mm. Since the properties of the ACC were confirmed to affect the cell performance at 80°C, the following section examines their effect up to the boiling point of water.

(a). I-V characteristics

(b). I-HFR characteristics

Fig.2. Experimentally obtained I-V and I-HFR characteristics at 80°C with different anode current collectors.

3.2 The effect of average pore diameter and thickness on the electrolysis cell performance up to the boiling point of water.

Fig. 3(a) and 3(b) show the effect of increasing the temperature to the boiling point on the electrolysis cell performance. I-V curves and I-HFR curves were measured at 80°C, 98°C, and 100°C at 0.1 MPa. When the temperature increases from 80°C to 98°C, the activation overvoltage decreases to a large extent as expected, but the ohmic overvoltage also decreases, which is estimated from the HFR in Fig. 3(b). The open circuit voltage (OCV) decreases only 50mV in the process of increasing the temperature from 80°C to 98°C corresponding to a 3 mV/°C increment. In addition, the OCV sharply decreases by an additional 60mV when the temperature continuously increases from 98°C to 100°C (about 30mV/°C) as shown in Fig. 3(a). Why the OCV decreases around the boiling point sharply will be studied in future research. Even though increasing the temperature from 98°C to 100°C induces a slightly higher ohmic overvoltage (2 mV at 2 A/cm²), the electrolysis voltage still decreases by about 8 mV at 2 A/cm². According to above experimental results, increasing the temperature up to the boiling point temperature improves the electrolysis cell performance without significant membrane dehydration.

(a). I-V characteristics

(b). I-HFR characteristics

Fig.3. Effect of increasing temperature from 80°C up to the boiling point on the electrolysis cell performance.

The effects of the ACC on the electrolysis voltage confirmed at 80°C are reexamined at the boiling point. Fig. 4(a) and 4(b) present the effect of thickness and average pore diameter on the electrolysis voltage and the HFR at 100°C and 0.1 MPa. When the temperature increases from 80°C to 100°C, the average pore diameter begins to significantly contribute to the electrolysis voltage. The effect of the average pore diameter on the I-V curves becomes more evident in Fig. 4(a) (about 30mV) than in Fig. 2(a) (less than 10mV). The I-HFR curves in Fig. 4(b) show that the smaller average pore diameter promotes the suppression of the ohmic resistance, indicating that the ACC with a small pore diameter can supply more water into the catalyst layer. The analysis in the section 3.1 at 80°C suggests that only the thickness of ACC affects the cell performance. However, the results at 100°C suggest that, in addition to the thickness, the average pore diameter also has an impact on the cell performance. At this temperature, less liquid water occupies the anode compared to 80°C. In this severe situation of water transport into the catalyst layer, the capillary-force-driven water transport is evidently enhanced by the smaller pore diameter.

At the boiling point, the thickness and the average pore diameter of the ACC affect not only the linear overvoltage (i.e., the ohmic overvoltage) but also the nonlinear overvoltage that consists of both the concentration overvoltage and the activation overvoltage. The Tafel plot shown in Fig. 4(c) clarifies which nonlinear component is affected by the properties of the ACC. The vertical axis on this figure is the IR-free voltage, which is calculated by subtracting the ohmic overvoltage from the electrolysis voltage. The same Tafel slopes of about 80 mV/decade are identified for the four titanium meshes (CC1-CC4) when the current density is less than 0.1A/cm², suggesting the same

activation overvoltage due to the same catalyst layer. When the current density is larger than 1 A/cm^2 , an additional nonlinear component is superimposed that can be attributed to the concentration overvoltage. The Tafel gradient of the concentration overvoltage is different for each of the four ACC materials, suggesting that the thickness and average pore diameter in the ACC greatly influences the electrolysis voltage by affecting the concentration overvoltage.

(a). I-V characteristics

(b). I-HFR characteristics

(c). IR-free Tafel plots

Fig.4. The effect of thickness and pore diameter at 100°C.

To investigate the effect of average pore diameter in detail and to find an optimized pore diameter, the effect of four of the different titanium meshes (CC3, CC4, CC4-3 and CC4-4) with different average pore diameters (35 μm , 21 μm , 15 μm and 10 μm) on the electrolysis cell performance is evaluated in Fig. 5(a) and 5(b). When the average pore diameter increases from 10 μm to 35 μm , the lowest electrolysis voltage and HFR appears at an average pore diameter of 21 μm (CC4), suggesting that an optimum average pore diameter exists in the range from 10 μm to 35 μm at 100°C. Again, the change in the HFR (ohmic resistance) in Fig. 5(b) cannot explain the change in the electrolysis voltage. Thus, the lowest electrolysis voltage obtained with the optimum pore diameter of 21 μm in CC4 is caused by suppressing both the concentration and the ohmic overvoltage from an sufficient water supply. According to the discussion in sections 3.1 and 3.2, CC4 is the optimum ACC material to minimize the electrolysis voltage.

Similar to the results shown in Fig. 4(c), the IR-free Tafel plots in Fig. 5(c) show that the average pore diameter influences the concentration overvoltage but not the activation overvoltage. In general, small pore diameters cause a large capillary force that is the main driving force for water transport through a hydrophilic ACC, where the hydraulic flow has less of a contribution. [37] However, small pore diameters will obstruct gas removal and increase the mass transport resistance. [4] Therefore, when the average pore diameter gradually increases from a small value, the concentration overvoltage should decrease at first and then increase. The optimum average pore diameter then occurs when the concentration overvoltage reaches its lowest value. In Fig. 5(c), the experimental results match the aforementioned expectations. With the average pore diameter in a range from 10 μm to 35 μm , the activation overvoltage of these four ACCs are the same because the Tafel slopes are the same up to 0.1 A/cm². But the lowest

concentration overvoltage appears at an average pore diameter of $21\mu\text{m}$ when the current density is larger than 1 A/cm^2 .

(a). I-V characteristics

(b). I-HFR characteristics

(c). IR-free Tafel plots

Fig.5. Effect of pore diameter at 100°C when the thickness is 0.2 mm.

3.3. The effect of contact angle on the electrolysis cell performance.

The effect of the contact angle on the electrolysis voltage and ohmic resistance is presented in Fig. 6(a) and 6(b). Three different titanium meshes (CC4-1, CC4-2 and CC4-3 in Table 2) are evaluated with the same characteristics (thickness, average pore diameter, etc.) except for the contact angle. The contact angle of CC4-1, CC4-2 and CC4-3 are 120°, 10°, and 0°, respectively, indicating that CC4-1 is hydrophobic, CC4-2 is hydrophilic, and CC4-3 is super hydrophilic. Fig. 6 shows that decreasing the contact angle suppresses both the electrolysis voltage and the ohmic resistance. The ohmic overvoltage difference, which is estimated from the ohmic resistance, is approximately 20 mV between CC4-2 and CC4-3 and 40mV between CC4-1 and CC4-2 at a current density of 2 A/cm², but the total electrolysis voltage difference at 2 A/cm² is about 100mV between CC4-2 and CC4-3 and 200mV between CC4-1 and CC4-2, respectively. Therefore, the overall electrolysis

voltage difference consists of not only a linear component but also a non-linear overvoltage component. Similar to the discussion in 3.1 and 3.2, a smaller contact angle suggests that the water supply to the anode catalyst layer is sufficient. According to Table 2, the contact angle of commercial titanium meshes are sufficiently small. Therefore, the effects of the contact angle, the thickness, and the average pore diameter indicate that the optimum ACC should be CC4 among the titanium meshes used in this study.

In addition, the Tafel plots with the IR-free voltage in Fig. 6(c) suggest that the contact angle of the ACC affects the concentration overvoltage. Similar to Fig. 4(c) and Fig. 5(c), the Tafel slopes of these three embedded meshes are also the same 80 mV/decade up to 0.1 A/cm², and Tafel gradients begin to show an apparent difference from 1 A/cm². Such a voltage difference reveals the difference in concentration overvoltage.

(a). I-V characteristics

(b). I-HFR characteristics

(c). IR-free Tafel plots

Fig. 6. Impact of wettability when the average pore diameter and thickness are 15 μm and 0.2 mm, respectively.

3.4. The optimum anode and cathode current collector combination

Fig. 7(a) and 7(b) show the effect of the different combinations of the anode and the cathode current collector. Conventionally, metal mesh or carbon paper is used as a cathodic current collector. [4-12] Thus, titanium mesh (CC4), SUS316L mesh (CC5), and SGL 34BA (CC6) are examined with the details of CC4, CC5 and CC6 found in Table 2. Three different combinations of the anode and the cathode current collector are noted as case1, case2 and case3. The I-V and I-HFR curves for case1 and case2 show the cathode current collector also has an effect on the electrolysis voltage. When the cathode current collector is changed from CC5 to CC6, the cell voltage at 1 A/cm² decreases from about 1.69 V to 1.59 V, which is ten times more than the ohmic overvoltage difference at 1 A/cm². When the cathode current collector is changed from CC5 to CC6, the evaporation of water at the boiling point is accelerated because CC6 (30 µm average pore diameter) has a smaller pore diameter than CC5 (60 µm average pore diameter). [27] As a result, the hydrogen gas can transfer into the flow channel with less resistance from the liquid water, and the concentration overvoltage caused by the transport of hydrogen gas is suppressed. [38]. Both the electrolysis voltage and the HFR decrease when the cathode current collector is changed from CC6 to CC4 (case2 and case3, respectively), which can be explained by their HFR difference.

Based on the previous discussion that showed that CC4 is the optimum ACC, CC4 used as both anode and cathode current collector performs at the lowest electrolysis voltage.

(a). I-V characteristics

(b). I-HFR characteristics

Fig.7. Electrolysis cell performance with different combinations of current collectors.

4 Conclusions

The effect of the porous properties (thickness, average pore diameter and contact angle) of the ACC on electrolysis performance at the boiling point of water was evaluated, and the following results were obtained:

- (1) Increasing the temperature up to the boiling point can improve the electrolysis cell performance while simultaneously avoiding significant membrane dehydration.
- (2) At the boiling point, the contact angle, the thickness, and the pore diameter of ACC affect the electrolysis voltage mainly through a change in the concentration overvoltage and the HFR value. Smaller contact angle and thinner ACC promise lowering the HFR value and concentration overvoltage in the range of 0-120° and 0.2-0.3mm.
- (3) The effects of the ACC properties on the electrolysis cell performance at 80°C are not entirely the same at 100°C. The effect of reducing the pore diameter on the electrolysis cell performance is not evident when the temperature is below the boiling point of water. However, when the temperature reaches the boiling point, the effect of the pore diameter becomes apparent with an optimum pore diameter of around 21 μm and in a range from 10 to 35 μm .
- (4) The cathode current collector also has an effect on the electrolysis voltage with the lowest electrolysis voltage obtained when both the anode and the cathode sides use CC4 (a thickness of 0.2 mm, a pore diameter of 21 μm , and a contact angle of 0° in water) as the current collector.

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