Performance Analysis of Hydrogen Generator using Cathode Feeding Method

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Abstract

Water supplied during polymer electrolyte water electrolysis is supplied to the anode where oxidation occurs to generate oxygen while hydrogen ions are moved into the cathode via passing through the electrolyte membrane to generate hydrogen through a reduction reaction. The hydrogen ions that pass through the electrolyte membrane are moved in a hydrated state, and so they play a role in the transportation of water molecules to the cathode side. To overcome these shortcomings, a water supply system installed at the anode side and a discharge water management system installed at the cathode side in an existing polymer electrolyte water electrolysis device were replaced. Instead, a water supply system only at the cathode side and a water supply system-type polymer electrolyte water electrolysis device whose components were optimized was used to recover the reduced energy efficiency-optimized components. Accordingly, energy efficiency reduction due to cathode feeding was observed when the current exceeded 3A, and this electric energy loss quickly increased the temperature of 50 cm³ cathode supply water, thereby maximizing the energy efficiency. Furthermore, the investigation results regarding the optimum shape of the flow-passage opening showed that a square shape was the most appropriate and that the most appropriate ratio of width between the opening and non-opening was approximately 2:1.

Keywords: Anode, Cathode, Hydrogen Generator, Oxygen, Titanium Plate

1. Introduction

In recent years, much attention has been paid to hydrogen because it can be used as a clean energy source, and in-depth studies on how to manufacture hydrogen efficiently are underway not only in Korea but also throughout the world. In conventional hydrogen manufacturing methods, fossil fuels such as methane gas are obtained by steam reforming, followed by refining them to produce hydrogen. However, a method using the electrolysis of water has been actively used to overcome environmental problems and the limited resources of fossil fuels in recent years.

As a method of obtaining hydrogen via the electrolysis of water, alkaline electrolysis is the most widely used method but it has many drawbacks. Hydrogen obtained through alkaline electrolysis has low purity and thus requires refining. Also, water-soluble electrolytes need continuous management, and there is the problem of device corrosion. In terms of performance, hydrogen obtained through alkaline electrolysis has low current density, which reduces efficiency as compared to the device size, and relatively high power consumption owing to high voltage with constant current. In contrast, polymer electrolyte water electrolysis, which has become more popular recently, overcomes most of the drawbacks of alkaline electrolysis. Hydrogen obtained through polymer electrolyte water electrolysis has no impurities except for a small amount of water, which requires no refining. Also, management of electrolytes is not necessary owing to the presence of a solid phase, and there is no device corrosion owing to the use of pure water. In terms of efficiency, it has a high current density and relatively low power consumption. Furthermore,
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Water electrolysis can occur well even at high pressure, which is an advantage for manufacturing high-pressure hydrogen without the need for compression devices. Water supplied to a polymer electrolyte water electrolysis device is supplied to the anode, where oxidation occurs to generate oxygen. At the same time, hydrogen ions are moved into the cathode via passing through the electrolyte membrane to generate hydrogen through a reduction reaction. The hydrogen ions that pass through the electrolyte membrane are in a hydrated state, and so they play a role in the transportation of water molecules to the cathode, thereby adding water on the cathode side. This additional water needs to be periodically discharged, which is inconvenient. It also increases the complexity of the device and consumes a significant amount of water at the anode side.

In this study, to overcome these shortcomings, the water supply system installed at the anode side and the discharge water management system installed at the cathode side in existing polymer electrolyte water electrolysis devices were replaced. Instead, the use of a water supply system only at the cathode side and a water supply system-type polymer electrolyte water electrolysis device whose components are optimized is proposed in order to recover the reduced energy efficiency-optimized components.

2. Principle of the Mechanism of Polymer Electrolyte Hydrogen Generator using Cathode Feeding Method

Figure 1 shows the material flow that is reacted and moved through the cross section of the membrane-electrode assembly in existing anode water supply methods. Water supplied to the anode emits oxygen and electrons as result of oxidation (2H₂O → O₂ + 4H+ + 4e−) at the catalyst surface, and hydrogen ions are moved to the cathode through the polymer electrolyte membrane. The hydrogen ions are moved in a hydrated state, thereby playing a role in transporting water at the anode side into the cathode. The hydrogen ions and electrons that arrive at the cathode generate hydrogen at the catalyst surface by means of a reduction reaction (4H+ + 4e− → 2H₂). The water that was transported with the hydrogen ions constantly accumulates at the cathode side, and thus a water discharge device is needed.

Figure 2 shows the material flow that is reacted and moved through the cross section of the membrane-electrode assembly using the cathode feeding method, in which the water accumulation problem in the cathode is resolved. With the cathode feeding method, water supplied to the cathode arrives at the anode catalyst surface through the polymer electrolyte membrane. Oxygen and electrons are emitted at the anode via an oxidation reaction. At the same time, hydrated hydrogen ions are moved to the cathode through the polymer electrolyte membrane. Hydrogen ions and electrons that arrive at the catalyst surface in the cathode generate hydrogen through a reduction reaction, and the water that was moved together with the hydrogen is discharged. Since the transported water was originally supplied from the cathode, no apparent changes are found. The water supplied to the cathode is reduced as much as the amount reduced due to water electrolysis only.
3. Performance Analysis on the Polymer Electrolyte Hydrogen Generator using Cathode Feeding Method

Figure 3 shows a schematic of the unit cell in the polymer electrolyte water electrolysis device using the cathode feeding method. The uppermost part is the cathode feeding supply water tank, which contains an appropriate amount of pure water. This water is sealed by a gasket and flowed down through the opening in the end plate at the cathode side. The water is sealed again by a gasket and flowed down through an opening in the titanium plate at the cathode side. This water is sealed again by a gasket and it enters into the cathode electrode, thereby generating hydrogen and oxygen through the process shown in Figure 2. The water in the bulk liquid state does not pass through the polymer electrolyte membrane, and water molecules arriving at the anode catalyst via diffusion are consumed completely by the water electrolysis reaction, which produces oxygen only through the opening in the titanium plate at the anode side.

As shown in Figure 3, the polymer electrolyte water electrolysis device using the cathode feeding method does not require management of discharge water at the cathode side, which resolves problems with existing polymer electrolyte water electrolysis devices that use an anode feeding method. The cathode feeding method reduces water consumption, which promotes a simple structure and miniaturization of the device. This not only reduces the manufacturing cost but also enables the convenient use of the device as a hydrogen generator module mounted in various systems. However, without overcoming the limiting low current density, which is a typical drawback of the cathode feeding method, a rapid increase in voltage can occur owing to the decreased water flow to the anode from the cathode when the current density is increased to increase hydrogen generation. If the device is run under these conditions, energy efficiency becomes very low and safety-related problems can occur as well. To solve these problems, we devised a method to increase the efficiency of the device by recovering most of the heat energy generated through electric energy loss during water electrolysis. The energy loss was converted into heat, which facilitates the water electrolysis reaction by minimizing the volume of the supply water tank and reducing the supply water.

Thus, most of the electric energy that is lost because of excessive voltage is converted into heat energy, and this heat energy increases the temperature of the supply water that is in contact with the electrode. Because the volume of the supply water is small, the temperature of the supply water quickly increases, which then maintains the contacted electrode temperature. Accordingly, the water moves more quickly and the energy efficiency increases due to the high temperature that is maintained at the membrane–electrode assembly. Since an increase in energy efficiency means reduced excessive voltage at a constant current density, the temperature of the supply water is not increased continuously; instead, it is stopped at a certain temperature.

The minimum energy needed in water electrolysis has 286 kJ/mol of enthalpy (equivalent to 1.48 V during water electrolysis) and 237 kJ/mol of free energy (equivalent to 1.23 V during water electrolysis), which is a difference of 49 kJ/mol (equivalent to 0.25 V during water electrolysis). This difference is a term that is related to entropy, which would be advantageous if it is supplied as heat energy. A Nafion® membrane used as a polymer electrolyte has the best ion conductivity at approximately 80°C, so that power consumption will be high owing to ohmic resistance if additional heaters are not used at room temperature. Therefore, if electric energy loss is converted into heat
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To confirm this, an additional water tank was connected to the water electrolysis device, as shown in Figure 4(a), and the water level was set between the inlet and outlet openings such that water electrolysis took place without water flowing, thereby deriving a relationship between voltage, current, and temperature. In addition, the water level in the additional water tank was increased, as shown in Figure 4(b), to facilitate water circulation according to the hydrogen movements, thereby comparing the water electrolysis results when a large amount of water was used.

As shown in Figure 5(a), the measurement results showed that the limiting low current density was overcome using cathode feeding and that highly reliability and high energy efficiency can be achieved by converting the recovered electric energy loss into heat energy. On the other hand, when the recovered electric energy loss was not converted into heat energy, a rapid increase in voltage occurred after exceeding 3 A, resulting in low energy efficiency. This difference can be related to the temperature change in the supply water, as shown in Figure 5(b).

The water electrolysis device using the cathode feeding method used in this experiment showed that a reduction of energy efficiency due to cathode feeding occurred when the current exceeded 3 A and that this

![Figure 4. Configuration of the water electrolysis performance test device. (a) No circulation type. (b) Circulation type.](image)

![Figure 5. Performance of the polymer electrolyte water electrolysis device using the cathode feeding method. (a) Voltage-Current curve. (b) Temperature-Current curve.](image)
electric energy loss quickly increased the temperature of 50 cm³ of the cathode supply water, thereby maximizing the energy efficiency.

4. Performance Analysis of Water Electrolysis According to Flow Passage Shape of Titanium Plates

In the polymer electrolyte water electrolysis device using the cathode feeding method, water movement should be optimized so that the supply water can reach the catalysis surface of the anode without problems. The supplied water enters the cathode electrode from the cathode side via a titanium plate. It is absorbed into the membrane–electrode assembly and then reacted and consumed at the anode catalysis surface. In the above process, hydrogen generated at the cathode can interrupt the supply water flow when it passes through the titanium plate. The titanium plate plays a role in not only supplying water and discharging hydrogen but also in uniformly supplying electrons to the cathode. Thus, for the titanium plate at the cathode side, it is necessary to design an optimized opening that can satisfy the above three functions.

The shapes of flow passages of titanium plates used in existing anode feeding polymer electrolyte water electrolysis devices are primarily circular with various diameters. In addition, mesh can be used instead of titanium plates. Mesh can have better fluid flow results, but it has a shortcoming in that gasket sealing and connection of the power supply is more difficult without a mesh. In the cathode feeding polymer electrolyte water electrolysis device proposed in this study, the water supply is more important than anode feeding. Therefore, a rectangular opening, which can facilitate water supply and hydrogen discharge, as well as supply electrons uniformly due to a relatively large area of the opening, was manufactured and compared with the shape and performance of circular openings. Furthermore, the effects of the relative dimensions of the opening and non-opening on performance were verified through experiments to determine the optimum dimensions.

<table>
<thead>
<tr>
<th>Type No.</th>
<th>Opening shape</th>
<th>Ratio of width between opening and non-opening</th>
<th>Ratio of area between opening and non-opening in the effective area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type 1</td>
<td>Square</td>
<td>2:1</td>
<td>0.8000:1</td>
</tr>
<tr>
<td>Type 2</td>
<td>Circular</td>
<td>2:1</td>
<td>0.5358:1</td>
</tr>
<tr>
<td>Type 3</td>
<td>Square</td>
<td>2:1.5</td>
<td>0.4848:1</td>
</tr>
</tbody>
</table>

Figure 6. Characteristics of titanium plates by flow-passage shape.

Three types of flow-passage titanium plates were designed, as shown in Figure 6 and Table 1, and performance experiments were conducted according to the flow-passage type. The effective area in Table 1 refers to the remaining area after the area blocked by the framework of the end plate used as the flat support of the flow passage plate is subtracted from the overall electrode area to which water is supplied.

The titanium plate shown in Figure 6 was connected as shown in Figure 3 and 20 cm³ of distilled water was poured into the water tank at the cathode side. Then, under the condition of no water flow, a voltage–current experiment was conducted according to the types of titanium plate listed in Table 1.

The results shown in Figure 7 revealed that Type 1 had very stable performance throughout the measurement section. This was because the square shape of the opening was sufficiently large, it satisfied the water supply needs, and it allowed for a uniform supply of discharge electrons of generated hydrogen simultaneously. Type 2 and Type 3 showed results similar to those of Type 1 in the low current density condition, but the voltage increased as the current density increased. This result was due to interference in the inter-fluid flow by the large amount of hydrogen generated, which was to some extent proportional to the current density. Water flow was interrupted by the
upwardly generated hydrogen flow through the opening because the opening area was significantly smaller than the non-opening, as shown in Table 1. Since the electron supply was carried via the non-opening, Type 2 and Type 3 had more advantageous conditions than Type 1. However, the non-opening areas of Type 2 and Type 3 were unnecessarily large given the experiment results because fluid flow became the factor that controlled the reaction as a current density increased.

Figure 7. Voltage-current result according to a flow-passage shape of the titanium plate.

On the other hand, in terms of just the opening area, there was no significant performance difference between Type 2 and Type 3, although Type 3, whose opening area was slightly smaller than that of Type 2, had a slightly better performance. This result indicates that not only the opening area but also its shape influenced the performance and that a square shape was more advantageous than a circular shape. The hydrogen generation at the cathode is a reduction process in which hydrogen ions are transferred via the polymer electrolyte membrane owing to electrons supplied from the non-opening. Thus, hydrogen generation at the surrounding area of the non-opening and opening will be promoted, whereas the center of the opening allows the passage of the supply water. For the circular opening, the surrounding area from which a sufficient supply of electrons is produced can be a virtual circular shape. Accordingly, the center of the opening, which allows the passage of supply water, can be a virtual circular shape as well. The square-shaped opening can also allow passage of supply water, so that it can be a virtual center square and the surrounding area from which a sufficient supply of electrons is produced will have a uniform width regardless of the shape. This is why a square-shaped opening is more advantageous than a circular-shaped opening for the virtual passage of supply water.

According to the above experimental results, the preferred opening shape is that of a square and the ratio of width between the opening and non-opening should be somewhat large; however, if this ratio is too large, the mechanical properties of the plate can decrease and the electron supply can become unstable. This would also present difficulties during manufacturing. Thus, we concluded that a ratio of 2:1 is an appropriate dimension.

5. Conclusion

In this study, to overcome these shortcomings, a water supply system installed only at the cathode side and a water supply system-type polymer electrolyte water electrolysis device whose components were optimized was proposed. Based on experimental results, we have come to the following conclusions:

- To overcome the rapid increase in voltage that occurs when increased current density is needed to increase hydrogen generation in the cathode feeding method, the volume of supply water was reduced by minimizing the volume in the supply water tank. This allowed most of the heat energy generated due to electric energy loss to be recovered immediately as heat, which increased the electric energy efficiency. The experiment results showed that as the current exceeded 3 A, a reduction in energy efficiency was observed due to cathode feeding, and this electric energy loss quickly increased the temperature of the supply water whose volume was less than 50 cm$^3$, thereby maximizing energy efficiency.
- The preferred opening shape by which the sufficient supply water reaches the catalysis surface of the anode is that of a square. The ratio of the width between the opening and non-opening should be somewhat large, but if this ratio is too large, the mechanical properties of the titanium plate can decrease and electron supply can become unstable. It would also present difficulties during manufacturing. Thus, we concluded that a ratio of 2:1 was an appropriate dimension.

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7. References