Proposal for a new system for simultaneous production of hydrogen and hydrogen peroxide by water electrolysis

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Accepted 2 February 2004

Abstract

Authors have proposed a new hydrogen production system that simultaneously produces hydrogen and hydrogen peroxide by water electrolysis. Experimental apparatus of the system is composed of a hydrogen electrode with platinum meshes, a hydrogen peroxide electrode with carbon material and an electrolyte with Nafion\textsuperscript{®}. In this paper, the superiority of the system is outlined, and the experimental results of the electrolytic synthesis of hydrogen and hydrogen peroxide from water are reported. Hydrogen peroxide is synthesized at the high efficiency when some kinds of carbon material are used as the hydrogen peroxide electrode. Furthermore, the possibility of applying the solar energy to this system is also discussed.

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Keywords: Hydrogen; Hydrogen peroxide; Water electrolysis

1. Introduction

At present, energy supply is mostly made up of fossil fuels. The fossil fuels have caused various global environmental problems such as acid rain and the global warming. These environmental pollutants, nitrogen oxides and sulfur oxide, in addition to a large amount of carbon dioxide, are discharged with the consumption of fossil fuels.

Researches for establishing new energy systems are being conducted in Japan. One of them is a World Energy Network project (WE-NET). In this project, hydrogen is produced by water electrolysis using electricity obtained from renewable energy sources that widely exist in the foreign countries, such as hydro-electricity, solar energy, geothermal energy, etc. The hydrogen is transported to Japan and it is utilized as fuel.

In the WE-NET project, research on the hydrogen production technology using a solid polymer electrolyte membrane is carried out (Eqs. (1)–(3)), and the conceptual design of the hydrogen production plant with 10 000 Nm\textsuperscript{3}/h is conducted [1].

\begin{equation}
2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2.
\end{equation}

(0.00 V vs. NHE).

Cathode : $4\text{e}^- + 4\text{H}^+ \rightarrow 2\text{H}_2$

(1.23 V vs. NHE).

\begin{equation}
\text{Anode} : 2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^-.
\end{equation}

As indicated in the above equations, oxygen is also produced with hydrogen. However, the effective use of the oxygen is not considered. On the assumption that a new water electrolysis system producing some useful chemical substances instead of oxygen is developed, the system seems to have various merits over the conventional system.
Hydrogen peroxide is a useful chemical substance for bleaching and sterilization of papers, pulp and natural fiber. The proportion of main application of hydrogen peroxide in Japan is shown in Table 1 [2]. The proportion of paper/pulp industry is the largest in application and it reaches 40%. Annual demand of hydrogen peroxide in Japan has reached 130,000–140,000 ton [2]. The price of the hydrogen peroxide (35% concentration) is about 80 yen/kg (1 dollar is about 107 yen in January 2004). Since the environmental loading of hydrogen peroxide is smaller than other bleaching agents, bleaching agents have shifted from chlorine and chlorine dioxide to hydrogen peroxide, oxygen and ozone in the pulp bleaching industry. A certain demand of hydrogen peroxide is expected in the future.

The auto-oxidation (AO) process discovered by Manchot is the most widely used for the synthesis of hydrogen peroxide [3,4]. This method is suitable for the mass production. In Japan, the hydrogen peroxide with the concentration over 50% is an object that gets subjected to the dangerous object law in the fire protection law, and transportation of this product is restricted. In order to make the transportation of hydrogen peroxide unnecessary, the research on the onsite hydrogen peroxide production method has been conducted all over the world [5–8]. Sudoh et al. [9,10] have examined the electrochemical production method of hydrogen peroxide. In the method peroxide ion is produced on the cathode of the electrolysis cell by the reduction of oxygen gas (Eqs. (1) and (4)). Characteristics of these three equations show that hydrogen and hydrogen peroxide can be produced simultaneously by water electrolysis.

2H₂O → HOOH + H₂.  \hspace{1cm} (7)

Cathode : 2e⁻ + 2H⁺ → H₂.  \hspace{1cm} (8)

Anode : 2H₂O → HOOH + 2H⁺ + 2e⁻  \hspace{1cm} (9)

(1.776 V vs. NHE).

We have made a comparison between our proposed system shown in Eqs. (7)–(9), the WE-NET system shown in Eqs. (1)–(3) and onsite hydrogen peroxide production system shown in Eqs. (4)–(6). In our proposed system, both one molecule of hydrogen gas and one molecule of hydrogen peroxide are produced by two-electron transfer. In the WE-NET system, only one hydrogen molecule is produced by two-electron transfer. In the onsite hydrogen peroxide production system, only one molecule of hydrogen peroxide is produced by two-electron transfer. Therefore, on the assumption that the electric current efficiency for electrolysis is equal in these three systems, our proposed system utilizes electricity more effectively than the other systems. It is summarized in Table 2.

The theoretically required voltage for the chemical reaction shown in Eq. (1) is 1.23 V. Actually, about 1.5–1.7 V is required for the reaction because of various voltage losses. About 1.7–2.0 V is required in the onsite hydrogen peroxide production system shown in Eq. (4). It is considered due to oxygen overpotential.

On the other hand, in our proposed system, there is the advantage that the oxygen overpotential need not be considered because there is no process which generates oxygen molecule on both electrodes. The theoretically required voltage for the chemical reaction shown in Eq. (7) is 1.776 V. On the assumption that the reaction shown in Eq. (7) proceeds at about 2.0 V, our proposed system produces hydrogen and hydrogen peroxide at lower electric power input in comparison with the conventional production technique shown in Eqs. (1) and (4). Characteristics of these three production techniques are summarized in Table 3.

<table>
<thead>
<tr>
<th>Application</th>
<th>Ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paper/pulp industry</td>
<td>40</td>
</tr>
<tr>
<td>Chemicals</td>
<td>30</td>
</tr>
<tr>
<td>Textile industry</td>
<td>8</td>
</tr>
<tr>
<td>Self consumption</td>
<td>22</td>
</tr>
</tbody>
</table>

Table 1
The proportion of main application of hydrogen peroxide

Table 2
H₂ and HOOH production with two-electron transfer

<table>
<thead>
<tr>
<th>Production method</th>
<th>H₂ production</th>
<th>HOOH production</th>
</tr>
</thead>
<tbody>
<tr>
<td>WE-NET</td>
<td>One molecule</td>
<td>None</td>
</tr>
<tr>
<td>Onsite HOOH production</td>
<td>None</td>
<td>One molecule</td>
</tr>
<tr>
<td>Our proposed system</td>
<td>One molecule</td>
<td>One molecule</td>
</tr>
</tbody>
</table>
Table 3
Characteristics of electrochemical production method of hydrogen peroxide and hydrogen

<table>
<thead>
<tr>
<th>Production method</th>
<th>Equation</th>
<th>Products</th>
<th>Oxygen generation</th>
<th>Voltage (theoretical/actual)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WE-NET</td>
<td>1</td>
<td>Hydrogen (Oxygen)</td>
<td>Yes</td>
<td>1.23/1.5–1.7</td>
</tr>
<tr>
<td>Onsite HOOH production</td>
<td>4</td>
<td>Hydrogen peroxide</td>
<td>Yes</td>
<td>0.6/1.7–2.0</td>
</tr>
<tr>
<td>Simultaneous production method of hydrogen and hydrogen peroxide from water</td>
<td>7</td>
<td>Hydrogen peroxide Hydrogen</td>
<td>No</td>
<td>1.77/(2.0)</td>
</tr>
</tbody>
</table>

Fig. 1. A schematic diagram of experimental apparatus for simultaneous production of H₂ and HOOH from water.

In our proposed system, oxygen evolution reaction at the anode shown in Eq. (3) becomes a competitive reaction for the hydrogen peroxide production shown in Eq. (9). As shown in Eqs. (3) and (9), the oxygen evolution reaction is more thermodynamically favorable than the hydrogen peroxide production. Therefore, the anode material that promotes the hydrogen peroxide production rate and inhibits the oxygen evolution reaction rate is required in order to realize our proposed system.

From above considerations, our proposed system is considered to be effective production system of hydrogen and hydrogen peroxide and an effective anode material is absolutely necessary for realizing this system.

3. Production cost estimation

In the WE-NET annual report of 2000, hydrogen production cost of the 1000 Nm³/h plant is estimated to be 28.4 yen/Nm³ [1]. In the estimation, 1.705 V of the electrolysis voltage and 5 yen/kW of electric power unit price are assumed, and the proportion of electric power cost in the manufacturing cost is estimated to be 73%. It is considered that the hydrogen electrode and the electrolyte of the conventional water electrolysis system can be applied to our proposed system. Therefore, on the assumption that the facility cost between WE-NET plant and our proposed system is not very different and our proposed electrolysis is conducted at 2.0 V, the production cost of 1 Nm³ of hydrogen and of 1.5 kg of hydrogen peroxide are roughly estimated to 32 yen (28.4 × 0.27 + 28.4 × 0.73 × 2.0/1.705). Since the hydrogen production cost by natural gas reforming is estimated to be 13.6 yen/Nm³ in the WE-NET annual report of 1998 [12], and since the trade price of hydrogen peroxide in North America is about 1.5 $/kg (100%) [13], our proposed system has a possibility of producing hydrogen and hydrogen peroxide at lower costs in comparison to the conventional production technique.

4. Experiments

A schematic diagram of the experimental apparatus for the simultaneous production of hydrogen and hydrogen peroxide from water is shown in Fig. 1. A commercially available DC voltage current source/monitor (Advantest Co. Model R6243) is used for monitoring electric current from the cell. The reaction time is 2 h and the current is monitored. In a series of experiments, the electrolysis voltage is set at 2.0 V in the first 1 h and set at 1.5 V in the next 1 h. The accuracy of DC voltage source is within 0.01% of setting voltage +300 μV. The reproducibility of DC voltage source is within 0.03% of setting voltage +600 μV. The accuracy of DC current monitor is within 0.01% of setting current +3.5 μA. The reproducibility of DC current monitor is within 0.03% of setting voltage +8 μA. All experiments are conducted at room temperature.
A commercially available sodium hydroxide aqueous solution (0.1 mol/l, Wako pure chemical industries, Ltd.) is used as anolyte solution and supplied to the anode. A commercially available tubing pump (MasterFlex®, model 7553-80) is used to supply the anolyte solution to the cell. The flow rate is kept at 1.0 ml/min. The precision of the flow rate measurement is within 2%. The cathode compartment is replaced with nitrogen gas. The gas chromatograph (Shimadzu, GC-8A) is used for the qualitative analysis of the hydrogen gas in the cathode compartment.

The concentration of hydrogen peroxide is determined by the permanganate method. A commercially available sulfuric acid (0.1 mol/l, Wako pure chemical industries, Ltd.) and potassium permanganate solution (0.1 mol/l, Wako pure chemical industries, Ltd.) are used for titration. The titration is carried out every 20 min.

A structure of the cell is shown in Fig. 2. The areas of the anode and the cathode of the cell both, are 4 × 4 cm². The thickness of the anode and the cathode is, both, 1 mm. Nafion® 115 (Du Pont Co.), which is one of polymer electrolytes, is used as the electrolyte. As cathode material, platinum meshes (Tanaka kikinzoku, 80 mesh) are used. Five kinds of carbon material (GF-20: Nippon carbon, FT300-25 and CH720-25: Kuraray chemical, CN211-20: Nippon Kynol, F-105: Kureha Chemical) are used as the anode material without any pretreatment.

5. Results and discussion

Figs. 3(1) and (2) show a time lapse of the current for the electrolysis using five kinds of carbon material as anode material. Figs. 3(1) and (2) are the same figures except for the scale of Y-axis. In the first 1 h of each experiment, the electrolysis voltage is set at 2.0 V and in the next 1 h it is set at 1.5 V.
Table 4

<table>
<thead>
<tr>
<th>Carbon material</th>
<th>Reaction time/min</th>
<th>Hydrogen production</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0–20</td>
</tr>
<tr>
<td>GF-20</td>
<td>1.9</td>
<td>32</td>
</tr>
<tr>
<td>FT300-25</td>
<td>20</td>
<td>1.0</td>
</tr>
<tr>
<td>CH720-25</td>
<td>33</td>
<td>0</td>
</tr>
<tr>
<td>CN211-20</td>
<td>2.1</td>
<td>47</td>
</tr>
<tr>
<td>F-105</td>
<td>4.6</td>
<td>18</td>
</tr>
</tbody>
</table>

A.C.: Average current/mA, C.E.: Current efficiency/\%.

In the cases of FT300-25 and CH720-25, an electric current larger than 50 mA is observed at the beginning of experiments in each case, then the current drops rapidly. The current observed in the next 1 h of experiments is much smaller than that observed in the first 1 h. On the other hand, in the cases of GF-20, CN211-20 and F-105, almost constant current is observed in the first 1 h in each case, and the difference of the current between the first and the next 1-h is much smaller than that of FT300-25 and CH720-25.

From the result of the titration of hydrogen peroxide, it is clarified that a certain quantity of hydrogen peroxide is synthesized in the cases of GF-20, CN211-20 and F-105. In the cases of FT300-25 and CH720-25, hydrogen peroxide is not detected. From the result of gas phase analysis in the cathode compartment, it is clarified that, in the condition that the electrolysis voltage is set at 2.0 V, a certain amount of hydrogen gas is produced in the cases of CN211-20, GF-20 and F-105, and hydrogen gas is not detected in the cases of FT300-25 and CH720-25.

The current efficiency of the simultaneous synthesis of hydrogen and hydrogen peroxide by the electrochemical reaction can be calculated from the monitored current value and the concentration of hydrogen peroxide obtained from the titration. The current efficiency is summarized in Table 4.

In the case of FT300-25 and CH720-25, it is considered that the measured current is not mainly caused from the water electrolysis. It is considered that the current is caused from the other phenomenon like an electric double layer capacitor or decomposition of functional groups on the carbon surface.

In the case of CN211-20, the current efficiency is about 50% of that in the condition electrolysis voltage is set at 2.0 V and no hydrogen peroxide is produced under the condition that the power is set at 1.5 V. In the case of F-105, the current efficiency is about 20% in the condition that the electrolysis voltage is set at 2.0 V, and no hydrogen peroxide is produced in the condition that it is set at 1.5 V. It is considered that, when CN211-20 or F-105 is used as the anode material, the reaction shown in Eq. (9) proceeds on the anode of the cell. On the other hand, in the case of GF-20, the current efficiency of about 30–50% is obtained during the experimental time. It is considered that, in this case, hydrogen peroxide may be produced in different reaction mechanism with the reaction formula shown in Eq. (9), because 1.77 V is theoretically required for the progression of the reaction.

It is considered that the remarkable differences among FT300-25, CH720-25, CN211-20, GF-20 and F-105 are...
Table 5
Estimation of an amount of H₂ and HOOH production

<table>
<thead>
<tr>
<th>Insolation</th>
<th>1000 W/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area of solar cells</td>
<td>10,000 m²</td>
</tr>
<tr>
<td>Efficiency of solar cell</td>
<td>10%</td>
</tr>
<tr>
<td>Efficiency of electrolysis</td>
<td>90%</td>
</tr>
<tr>
<td>Voltage for electrolysis</td>
<td>2.0 V</td>
</tr>
<tr>
<td>Amount of H₂</td>
<td>2.3 mol/s</td>
</tr>
<tr>
<td>Amount of HOOH</td>
<td>2.3 mol/s</td>
</tr>
</tbody>
</table>

caused from the difference of surface condition of these carbon materials. It is necessary to examine the difference in detail in order to get the strategy to improve the reaction rate and current efficiency.

6. H₂ and HOOH production by water electrolysis utilizing renewable energy sources

As an application of our proposed system, we have estimated the amount of hydrogen and hydrogen peroxide when renewable energy is used as energy source. Fig. 4 shows a conceptual scheme of the system. In this figure, solar cells are assumed. Under this condition, we have roughly estimated the amount of hydrogen and hydrogen peroxide production. The condition for the estimation and the result are summarized in Table 5. As indicated in the table, a certain amount of hydrogen and hydrogen peroxide can be produced from water.

The theoretically required voltage for simultaneous production of hydrogen and hydrogen peroxide is 1.776 V. Therefore, the light with the wavelength shorter than 698 nm is applicable in order that the reaction proceeds with photocatalysts. If low-priced photocatalysts functioning in visible range is prepared, it is considered that hydrogen and hydrogen peroxide can be produced directly from solar energy. We will inquire the photocatalyst for the reaction.

7. Conclusions

Authors have proposed the new production system that simultaneously produces hydrogen and hydrogen peroxide by water electrolysis. From the production cost estimation, it is seen that in the new system hydrogen and hydrogen peroxide costs are lower in comparison with the conventional production technique. The experimental results in laboratory scale show that hydrogen peroxide and hydrogen gas can be produced using certain types of carbon material as anode material. Although the current efficiency and the current value are not sufficient to practical use, it is necessary to give the details of the mechanism of this reaction clear. It has to be noted that possibility of a new hydrogen production system by water electrolysis is experimentally shown.

References