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A novel deuterium separation system by the combination of water electrolysis and fuel cell

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Abstract

A new electrolytic deuterium separation system using a fuel cell has been proposed. It is found by calculation that the new system remarkably reduces energy consumption for heavy water production by reusing the hydrogen and oxygen gases at a fuel cell. However, the production cost is more expensive than that of the GS process which utilizes inexpensive heat energy. When voltage efficiencies of both the water electrolysis and the fuel cell exceed 87%, the new system will become a profitable process.
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1. Introduction

Practical plants for deuterium separation have been operated by the dual temperature water–hydrogen sulfide exchange process (GS process) and the water distillation process at the final stage. However, the GS process has many problems. Hydrogen sulfide is toxic and corrosive, energy consumption is high and plant size is large due to the low separation factor. Therefore, many researchers have studied new separation processes as alternatives to the GS process [1–6].

Although the water electrolysis process was mainly used for heavy water production since the 1930s [5], it is no longer used except in the final separation stage. The reason is that water electrolysis consumes an enormous amount of the electric energy for a large-scale production at the primary

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Nomenclature

A	quantity of feed water (mol)
E_{Fuel}	power generation at fuel cell (kW h)
E_{Total}	total power consumption for D_2O production (kW h)
E'_{Total}	total power consumption per kg of D_2O production (kW h kg^{-1})
E_{Water}	power consumption at water electrolysis (kW h)
H	total flow of water recycled by fuel cell (mol)
i	stage number (–)
M_{c1}	construction cost per kg of D_2O production ($ kg^{-1})
M_{c2}	fuel cell introduction cost per kg of D_2O production ($ kg^{-1})
M_o	operation cost per kg of D_2O production ($ kg^{-1})
M_t	total cost per kg of D_2O production ($ kg^{-1})
N	minimum stage number (–)
P	quantity of heavy water products (mol)
V	theoretical decomposition voltage of water (V)
x_A	deuterium atomic fraction in feed water (–)
x_i	deuterium atomic fraction in water leaving stage i (–)
x_P	deuterium atomic fraction in products water (–)
y_i	deuterium atomic fraction in hydrogen gas (–)
α	separation factor (–)
η_w	voltage efficiency of water electrolysis (–)
η_f	voltage efficiency of fuel cell (–)

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separation stage. However, if energy consumption is considerably reduced, the electrolysis process is still attractive due to the highest separation factor and the lack of pollutive exhausts. Moreover, the water electrolysis process can be applied for tritium recovery. In the conventional electrolysis process, no attempts have been made to recover energy from the gases evolved from the water electrolysis cell. Therefore, if the evolved hydrogen and oxygen gases are fed into a fuel cell, a large amount of energy will be recovered as electricity. Based on this novel concept, the authors propose a new deuterium separation system by using a fuel cell.

In a previous paper [7], a new electrode material having high deuterium separation factor was developed. The deuterium separation factor, α, is defined by the following isotopic abundance ratio

$$\alpha = \frac{\left(\frac{[D]}{[H]}\right)_l}{\left(\frac{[D]}{[H]}\right)_g} \tag{1}$$

where [D] and [H] are atomic fractions of deuterium and protium, the subscript l refers to the liquid phase and g to the gas phase. By using an iron electrode prepared in a magnetic field, the value of α was maximally 12.3 which is much higher than that of mild steel ($\alpha = 5$–9) used in conventional plant. This high factor value is expected to reduce not only energy consumption but also construction cost owing to the decrease in number of stages.

In this paper, the new cascade system is proposed as a substitute for the GS process and is discussed considering energy consumption and economics.

2. Theory

Depending on the deuterium concentration at each stage, the total system is divided into two types of cascade, 'simple cascade' and 'recycle cascade'. In this section, electric power consumption is calculated for each cascade.

2.1. Simple cascade

The simple cascade is used in the lower stages where the tail stream has too little deuterium to warrant conducting deuterium recovery. In the conventional simple cascade, no attempt is made to reprocess hydrogen and oxygen gases evolved from each electrolytic cell.

The new cascade system is expected to reduce power consumption remarkably by recycling such evolved gases. As shown in Fig. 1, both hydrogen and oxygen gases are supplied to the fuel cell for generating electric power. The electricity is returned to the electrolysis cell, and the water produced is wasted into the atmosphere. In this figure, the flow chart at the new simple cascade is also illustrated,
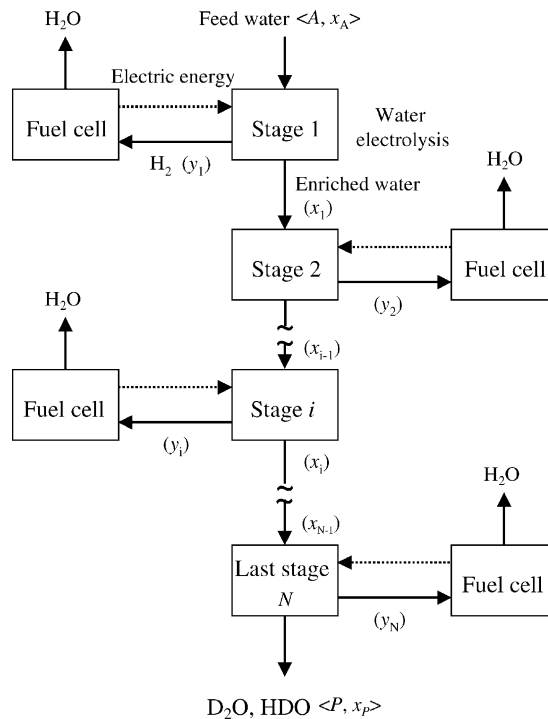
Fig. 1. Schematic illustration of steady-flow simple cascade using fuel cell.

where A is the quantity of feed water, P is the quantity of product water, x_A is the atomic fraction of deuterium in the feed water and x_P is the atomic fraction of deuterium in the product water.

Power consumption at the electrolysis process, E_{Water}, is given as

$$E_{Water} = (A - P)W_{Water} \tag{2}$$

where W_{Water} is power consumption per mol of water and is calculated as follows

$$W_{Water} = \frac{2FV(1/\eta_w)}{Z} \tag{3}$$

where F is the Faraday constant, V is the theoretical decomposition voltage of water, η_w is the voltage efficiency of water electrolysis and Z is the conversion factor (3.60×10^9/CV[MW h]$^{-1}$) [5].

If the evolved hydrogen and oxygen gases are totally reused in the fuel cell, power generation at the fuel cell, E_{Fuel}, is given as

$$E_{Fuel} = (A - P)W_{Fuel} \tag{4}$$

where W_{Fuel} is the power generation per mol of water generation and is calculated as follows

$$W_{Fuel} = \frac{2FS\eta_f}{Z} \tag{5}$$

where η_f is the voltage efficiency of fuel cell.

From Eqs. (2) and (4) total power consumption, E_{Total}, is expected to be

$$E_{Total} = E_{Water} - E_{Fuel} = \frac{2F}{Z}(A - P)V\{(1/\eta_w) - \eta_f\} \tag{6}$$

2.2. Recycle cascade

The recycle cascade is used when the depleted deuterium content in hydrogen gas has sufficient value to warrant reprocessing. In the conventional recycle cascade, the gases evolved from the electrolysis are recombined in a burner, and the resulting water vapor is condensed and fed to a lower stage.

In the new cascade system, the burner is replaced by a fuel cell as shown in Fig. 2. The electric power generated at the fuel cell is returned to the electrolysis cell and the resulting water is fed to a lower stage.

In the present research, 'ideal cascade model' [5], which is easy to treat theoretically, is used to calculate power consumption. The ideal cascade defines that α is constant through all stages and the head stream and tail stream fed to each stage have the same composition, $x_{i-1} = y_{i+1}$, which means that deuterium enrichment at the fuel cell is not considered in the present calculation.

Power consumption by water electrolysis is given as

$$E_{Water} = (A - P + H)W_{Water} \tag{7}$$

where H is the total flow of water recycled at all fuel cells and is given as [5]

$$H = \frac{P}{\alpha^{0.5} - 1} \left\{ \frac{[x_P(\alpha^{0.5} + 1) - \alpha^{0.5}]\ln[x_P(1 - x_A)/x_A(1 - x_P)]}{\ln \alpha^{0.5}} + \frac{(x_P - x_A)}{x_A(1 - x_A)} \frac{[\alpha - (\alpha + 1)x_A]}{\alpha^{0.5} - 1} \right\} \tag{8}$$
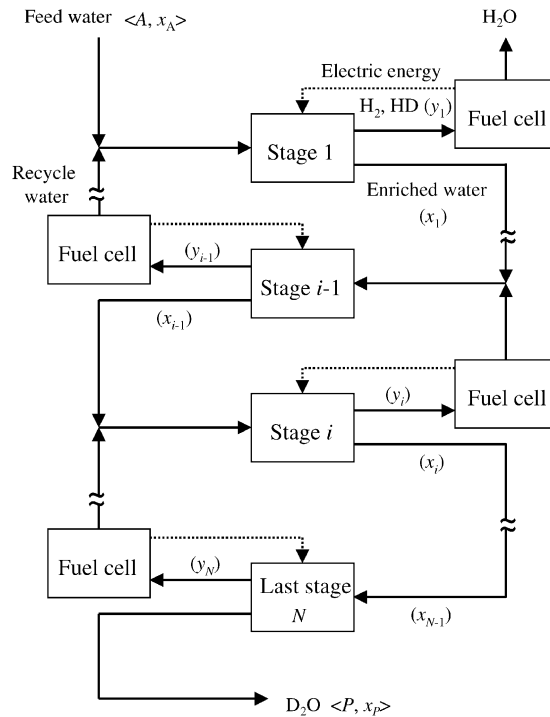
Fig. 2. Schematic illustration of steady-flow recycle cascade using fuel cell.

If the evolved gases are totally reused in fuel cell, E_{Fuel} is given as

$$E_{Fuel} = (A - P + H)W_{Fuel} \tag{9}$$

From Eqs. (7) and (9), E_{Total} at the new recycle cascade is given as

$$E_{Total} = \frac{2A}{Z}(A - P + H)V\{(1/\eta_w) - \eta_f\} \tag{10}$$

3. Calculation and discussion

3.1. Energy consumption

As a model case, the authors consider a plant to produce heavy water by the new cascade system using alkaline fuel cell. The plant consists of the simple cascade at lower stages and the recycle cascade at upper stages.

The value of x_A is taken as the natural value of 0.000149, and the value of x_P is taken as 0.998 which value is necessary for the heavy water nuclear reactor. The value of A is taken as 10,000 mol. The value of α is taken as 12.3 [7], which can be attained by using an iron electrode prepared in a magnetic field. Regardless of the deuterium concentration, the voltage of water electrolysis is taken as 1.60 V ($\eta_w = 0.75$) [8] and the voltage of the fuel cell is taken as 1.00 V ($\eta_f = 0.85$) [9] at all stages, where the theoretical decomposition voltage, S, is taken as 1.18 V at 80 °C.

Table 1
Calculation values using the new deuterium separation system ($\alpha = 12.3$)

Stage no.	Deuterium atomic fraction in each stage		Hydrogen recycled from higher stages, H (mol)	Products, P (mol)	Power consumption, E'_{Total} (MW h kg^{-1})
	Hydrogen, y	Water, x			
Feed		0.000149			
1	0.0000425	0.000522			
2	0.000149	0.00183	4490	1.07	21.1
3	0.000522	0.00639	893	0.830	20.3
4	0.00183	0.0220	202	0.646	24.6
5	0.00639	0.0733	48.2	0.503	32.0
6	0.0220	0.217	12.9	0.391	39.8
7	0.0733	0.493	4.38	0.304	51.0
8	0.217	0.773	1.95	0.237	65.5
9	0.439	0.923	1.00	0.184	84.7
10	0.773	0.977	0.509	0.143	108
11	0.923	0.993	0.232	0.112	138
12	0.977	0.998	0.0816	0.0889	174

The minimum stage number at the ideal cascade model, N, is given by the following equation [5]

$$N = 2\frac{\ln[x_P(1-x_A)/(1-x_P)x_A]}{\ln\alpha} - 1 \tag{11}$$

It is found that 12 stages ($N = 11.9$) are necessary for the new cascade system, while 16 stages ($N = 15.3$) are needed for the conventional mild steel ($\alpha = 7$). This suggests that the present system can eliminate 25% of construction costs.

To determine which stage is the most desirable to start recycling the hydrogen in terms of energy consumption, calculations were conducted and the results are summarized in Table 1. In the first column, stage no. is listed. The deuterium concentration at each stage is obtained from the following equations [5]

$$x_i = \frac{\alpha^{i/2}x_A}{\alpha^{i/2}x_A + 1 - x_A} \tag{12}$$

$$y_i = \frac{\alpha^{(i-2)/2}x_A}{\alpha^{(i-2)/2}x_A + 1 - x_A} \tag{13}$$

where the atomic fraction of deuterium in water at stage i is x_i and the fraction in hydrogen gas at stage i is y_i. In the third column, total recycled hydrogen is given when the recycle cascade starts from the corresponding stage. The fourth column means total products when the recycle cascade starts from the corresponding stage. In the last column, the total power consumption per kg of heavy water, E'_{Total}, is listed when the recycle cascade starts from the corresponding stage. From the calculation, it is found that the smallest value of about 20 MW h kg^{-1} is attained when the recycle cascade starts from stage no. 3.

Taking the performance of alkaline fuel cells into account [9], it can be assumed that flow rates of the gases evolved from water electrolysis and those consumed at the fuel cell are equal. The fuel cell is
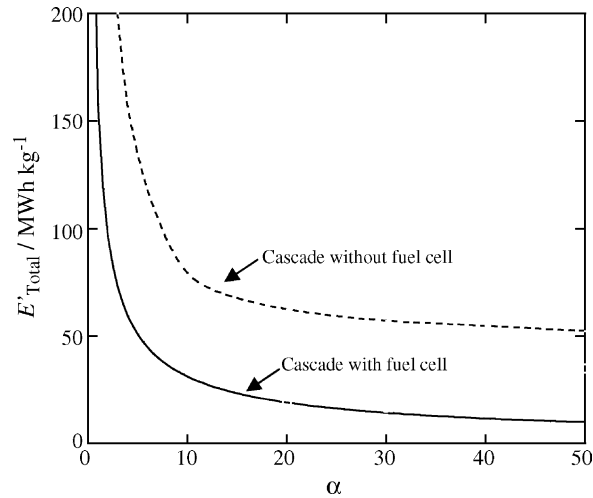
Fig. 3. Dependence of E'_{Total} on separation factor in the conventional and the new cascades (broken line, cascade without fuel cell; solid line, new cascade with fuel cell).

directly connected to the electrolysis cell without any compressors since the fuel cell can work at a low pressure (about 1 bar) at 80 °C.

Fig. 3 shows the dependence of E'_{Total} on the separation factor, α. In the figure, the broken line stands for the conventional cascade without fuel cell and the solid line does for the proposed new cascade with fuel cell, respectively. In the conventional electrolysis, E'_{Total} significantly increases with the decrease of α (≤ 10). When mild steel ($\alpha = 7$) is used without a fuel cell, E'_{Total} is about 100 MW h kg^{-1}. When mild steel is used for water electrolysis combined with a fuel cell, E'_{Total} is reduced to about 40 MW h kg^{-1}. Moreover, when the new iron electrode ($\alpha = 12.3$) is used for water electrolysis combined with a fuel cell, E'_{Total} is further reduced to about 20 MW h kg^{-1}.

Fig. 4 shows E'_{Total} values for various deuterium separation processes. The water distillation process consumes the highest energy of about 170 MW h kg^{-1} [5] and the conventional electrolysis process uses about 100 MW h kg^{-1}. The GS process uses about 30 MW h kg^{-1} [10]. The new cascade system requires the smallest energy of about 20 MW h kg^{-1}.

3.2. Economics

Firstly, the production cost of the GS process is estimated with reference to the Laprade Heavy Water Plant in Canada [11]. The construction cost and the operation cost are estimated, respectively. Since the construction cost is reported to be about $ 800 million, the unit investment cost, M_{c1}, of the plant capable of producing annually 600 t-D_2O is calculated as follows

$$M_{c1} = \frac{8.00 \times 10^8 \ (\$)}{6.00 \times 10^2 (\text{t year}^{-1}) \times 10^3 (\text{kg t}^{-1}) \times 20 \ (\text{year})} = 66.7 \ (\ \text{kg}^{-1}) \qquad (14)$$

where the interest is neglected and the depreciation is assumed to be 20 years. The operating cost, M_o, is reported to be about 95.0 $ kg^{-1} as the sum of electricity cost of 13.0 $ kg^{-1} and steam cost of 82.0 $ kg^{-1}. It should be noted that M_o does not include maintenance costs such as labor and materials.
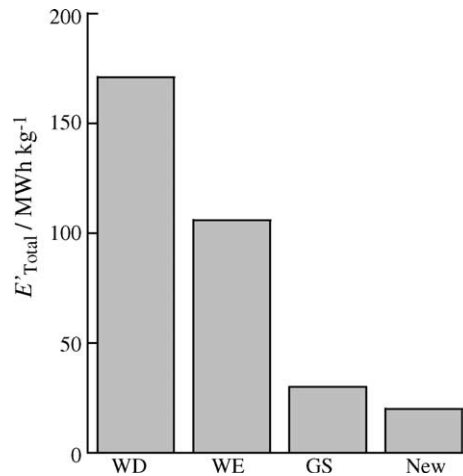
Fig. 4. Comparison of energy consumption, E'_{Total}, for various deuterium separation processes (GS, GS process; New, new cascade process; WD, water distillation process; WE, water electrolysis process).

Thus, the total cost per kg of heavy water production, M_t, is

$$M_t = M_{c1} + M_o = 66.7 + 95.0 = 161.7 (\$\,\text{kg}^{-1}) \tag{15}$$

Secondly, the production cost of the new system is estimated. The unit investment cost, M_{c1}, of the water electrolysis plants is estimated from the alkaline water electrolysis plant in the WE-NET project in Japan [12]. The plant costs $ 140 million and electrolyzed water at about 1.43×10^7 mol h^{-1}. In this plant, heavy water production is calculated to be about 200 t year^{-1} since the new cascade system can produce 0.83 mol heavy water by 10,000 mol feed water as shown in Table 1. When the depreciation is also assumed to be 20 years, M_{c1} is given as

$$M_{c1} = \frac{1.40 \times 10^8 \ (\$\ )}{2.08 \times 10^2 (\text{t year}^{-1}) \times 10^3 (\text{kg t}^{-1}) \times 20 (\text{year})} = 33.6 (\$\,\text{kg}^{-1}) \tag{16}$$

The new cascade process needs 20.3 MW h kg^{-1}, as shown in Table 1. If the electricity costs 17.0 $ MW h^{-1}, M_o is given as

$$M_o = 20.3 (\text{MW h kg}^{-1}) \times 17.0 (\text{MW h}^{-1}) = 345 (\$\,\text{kg}^{-1}) \tag{17}$$

Furthermore, the new cascade needs extra cost for the fuel cell introduction. The power generation, E_{Fuel}, is obtained from Eq. (9)

$$E_{\text{Fuel}} = 1.52 \times 10^7 (\text{mol h}^{-1}) \frac{2 \times 9.65 \times 10^4 (\text{C mol}^{-1}) \times 1.18 (\text{V}) \times 0.85}{3.6 \times 10^6 (\text{C V}[\text{kW h}]^{-1})} = 8.17 \times 10^5 (\text{kW}) \tag{18}$$

Since alkaline fuel cells cost 100 $ kW^{-1}, the unit investment cost, M_{c2}, is given as

$$M_{c2} = \frac{8.20 \times 10^5 (\text{kW}) \times 10^2 (\$\ \text{kW}^{-1})}{2.08 \times 10^2 (\text{t year}^{-1}) \times 10^3 (\text{kg t}^{-1}) \times 20 (\text{year})} = 19.7 \ (\$\,\text{kg}^{-1}). \tag{19}$$
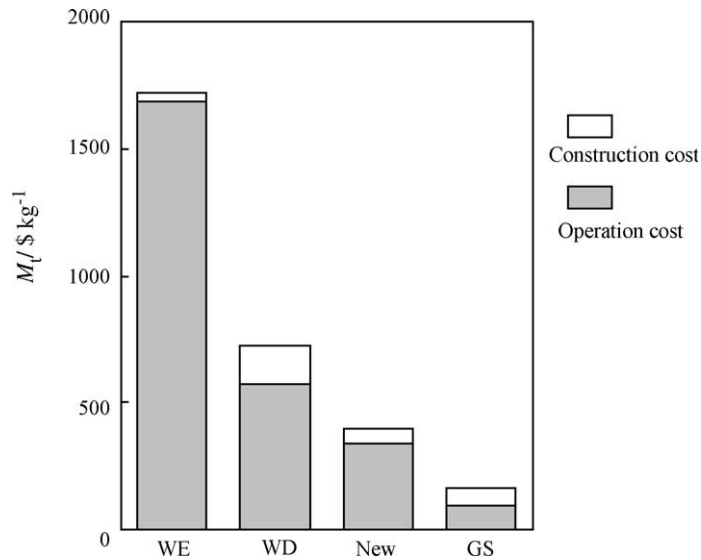
Fig. 5. Comparison of heavy water production cost, M_t, for various deuterium separation processes (GS, GS process; New, new cascade process; WD, water distillation process; WE, water electrolysis process).

Then, M_t is given as

$$M_t = M_c + M_o + M_f = 33.6 + 345 + 19.7 = 398.3 \, (\text{kg}^{-1}) \tag{20}$$

In the same manner, heavy water production costs are estimated for the conventional electrolysis process and the water distillation process [5]. Fig. 5 shows a comparison of M_t for various separation processes. The production cost of the new cascade system can be reduced to one fourth, compared with the conventional electrolysis process. However, M_t of the new cascade is still more expensive than that of the GS process. This is mainly due to the difference in the unit energy price. That is, the GS process utilizes cheap steam energy while the new process needs the more expensive energy of electricity.

In spite of the above evaluation, it should be noted that the new cascade system has a remarkable advantage that can be applied for tritium recovery. In a heavy water reactor, tritium is accumulated in heavy water during the operation by the nuclear reaction. Tritium separation from the heavy water is necessary to recover the heavy water, diminishing the radioactive waste and reducing the environmental burden [13]. Several processes for such tritium recovery have been developed [13–15], e.g. distillation, chemical exchange, catalytic exchange and water electrolysis. The new cascade system has the advantages that the method has a high separation factor and can be performed in small instruments.

Finally, it is worth considering the target of the voltage efficiencies for both water electrolysis and fuel cells for the new process to be favorable in payability. Since heavy water costs 300 $ kg^{-1} at the present [11], let the target price be 200 $ kg^{-1}. From Eq. (10), the voltage efficiencies of water electrolysis and fuel cell are obtained and plotted in Fig. 6. From the figure, when the efficiencies of both electrolysis and fuel cell exceed about 87%, respectively, the present system can be more profitable than the GS process.

Finally, it is noted that the present new system can be applied also for the tritium recovery.
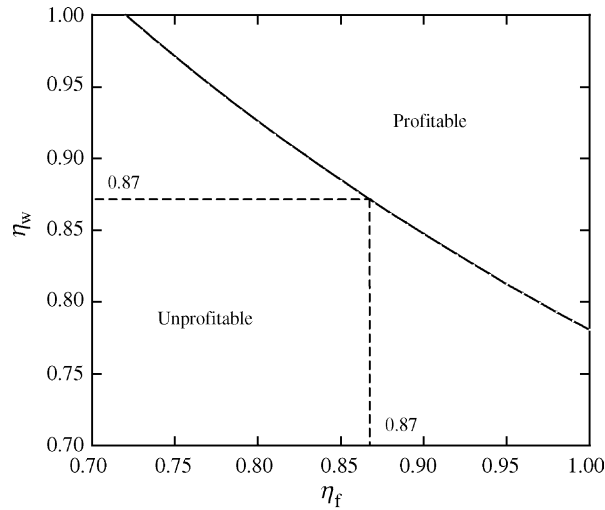
Fig. 6. Relationship between voltage efficiency of water electrolysis and fuel cell when the cost of heavy water production is 200 \$ kg^{-1} ($\alpha = 12.3$, $S = 1.18$ V).

4. Conclusions

In this paper, the new deuterium separation system using a fuel cell is proposed as a substitute for the GS process and is investigated from the viewpoints of energy consumption and economics.

(1) By using the new electrode having a high separation factor, the process is reduced to 12 stages for the new cascade system from 16 stages for the conventional electrolysis system.
(2) The production cost of the new cascade system is about one fourth, compared with the conventional electrolysis process.
(3) The production cost was estimated as about 380 \$ kg^{-1}, which was more expensive than that of the GS process. This is mainly due to differences in the unit energy price.
(4) When the voltage efficiencies of water electrolysis and fuel cell exceed 87%, respectively, the new system can be more profitable than the GS process.

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