Efficient hydrogen production through the thermochemical IS process using membrane technologies
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ABSTRACT
The IS process is one of water splitting methods to produce hydrogen using I2 and SO2 as catalysts. Three kinds of membrane techniques (Hydrogen permselective membrane reactor for HI decomposition reaction (HPMR), Electro-electrodialysis for concentration of HI (EED), Electrochemical cell for the reaction of SO2, I2 and H2O (EC)) were investigated by viewpoints of the total thermal efficiency. The HI concentration procedure by EED was the best method to improve thermal efficiency. The maximum thermal efficiency was 40.8 % at 12.5 mol kg-1H2O of HI concentration after EED. Thermal efficiency for the EC was slightly lower than that for EED by using the electrochemical data we had obtained. However, this method has a potential for the simple process operation compared with EED. In order to obtain higher thermal efficiency by featuring the EC, about 30 % of the required electric energy demand should be reduced. Total thermal efficiency can be improved only by 1 % for HPMR, and this technique should be applied to help material stabilities after HI decomposition reaction.

KEY WORDS
hydrogen production, thermochemical water decomposition, IS process, membrane technologies

INTRODUCTION
There have been many hydrogen production methods studied for the future energy system. The thermochemical water splitting IS process is one of the water decomposition methods to produce hydrogen to decrease the decomposition temperatures of water (ca. 4300 K) using some recycling agents. Figure 1 shows the simple schematic diagram of the IS process. The IS process mainly consists of three reactions. One is the Bunsen reaction (2H2O + I2 + SO2 = 2HI + H2SO4) where water reacts into two kinds of acids. These acids are vaporized, and decomposed into H2 and O2 from HI and SO3 (H2SO4), respectively. I2 and SO2 are recycled to the Bunsen reaction. As a result, the total reaction through the process is H2O = H2 + 0.5O2. The maximum required temperature in the process (ca. 1100 K) is the decomposition reaction of SO3. Kasahara et al. (2003, 2004a) reported that thermal efficiency to
produce hydrogen was 56.8 % under the ideal conditions of the IS process by heat/mass balance evaluations on the HI concentration and decomposition procedures. The IS process was demonstrated at the rate of 31.5 L-H2 h⁻¹ for 20 h by using the glass-made apparatus (Kubo et al., 2004). In order to realize the IS process, the recycle processes should be operated efficiently. There are three kinds of membrane techniques proposed to improve the IS process. One is electro-electrodialysis (EED) to concentrate HI solution using cation exchange membrane (Hwang et al., 2003). This is indicated as the gray part of No.2 in Figure 1. Concentration procedure of HI before HI distillation is very important, because much amounts of water vapor is introduced to HI decomposer by the azeotropic compositions of HI. The azeotropic concentration of HI is only ca. 15 %, and about 85 % of the obtained vapor in HI distillation column will be steam. Heat demands for water evaporation can be reduced by the concentration of HI over the azeotropic concentration of HI through the EED. Second is application of hydrogen permselective membrane reactor (HPMR, No.3 in Figure 1) at the decomposition reaction of HI (Nomura et al., 2004a). The reaction equilibrium of the HI decomposition is only 22 % at 723 K, and unreacted HI should be recycled to the decomposer. 76.8 % of the decomposition conversion of HI was obtained by using the hydrogen permselective silica membrane prepared by a chemical vapor deposition method. Third is the application of electrochemical cell (EC, No.1 and No.2 in Figure 1) featuring a cation exchange membrane to the Bunsen reaction. The two acids solutions obtained at the Bunsen reaction had been separated in a liquid-liquid separator by adding excess amounts of I₂ and H₂O. These I₂ and H₂O should be separated at the later procedures. In the former literature (Norman et al., 1981), 8 mol of I₂ and 10 mol of H₂O were added to produce 1 mol of H₂. The excess amount of I₂ and H₂O were reduced to 1.9 mol and 3.1 mol by the application of the EC (Nomura et al., 2004b). EC is a combination of an acids separator and concentrator. Each membrane techniques improved the IS process, however, it is not clear the effects of the applications of the membrane techniques on the total thermal efficiency. The evaluations were conducted only on the HI concentration and decomposition system (Kasahara et al. 2003, 2004a, Nomura et al. 2004a, b). In this report, effects of these membrane techniques on the IS process were evaluated by the heat/mass balance calculations for both HI and H₂SO₄ system. Especially for EC, the operating conditions were optimized by I-V evaluation of the cell. The properties of the membrane techniques were clearly discussed from the thermal efficiency to produce hydrogen.
EXPERIMENTALS

The experimental data in the literature were used for the discussions of the EED (Hwang et al., 2003) and HPMR (Nomura et al., 2004a). In this report, only experimental data for the EC were shown for the discussions. Figure 2 shows the schematic diagram of the EC for the Bunsen reaction. Anode side of the cell and cathode side of the cell were divided by a cation exchange membrane. Nafion 117 (Dupont) was employed for the membrane with the effective membrane area of 5.06 x 10^{-4} m^2. Pure SO_2 (Sumitomo Seika Co.) was introduced into H_2SO_4 solution by bubbling for anolyte. The reaction at the anode electrode is “SO_2 + 2H_2O = H_2SO_4 + 2H^+ + 2e^-”. At the cathode side, the electrode reaction is “I_2 + 2e^- = 2I^-”. H^+ was permeated through the cation exchange membrane, and HI is obtained in the catholyte. The total reaction is “2H_2O+I_2+SO_2= 2HI+H_2SO_4” that is the same to the Bunsen reaction. Temperature of the cell was controlled at 313 K by the heaters placed at the outside of the electrodes. Cell current was controlled by Potentiostat/Galvanostat HA-305 (Hokuto Denko). The concentration of each component was measured by titration using Comtite COM-900 (Hiranuma Co.). The detailed experimental procedures were described in the literature (Nomura et al. 2004b).

CALCULATIONS

Thermal efficiency to produce hydrogen was calculated based on heat/mass balance of the total process. The detailed calculation procedures were shown in elsewhere (Kasahara et al. 2004b). H_2 production rate was fixed at 1 mol s^{-1}. Mass flow around HI decomposer was calculated by deciding HI conversions. Mass flow around HI distillation was decided by liquid vapor equilibrium of HI, I_2 and H_2O solutions and HI composition after HI concentrator. Four stages vaporizer was employer for H_2SO_4 concentration and decomposition procedures. Energies for pumping were not considered for the evaluation. Heat balance was calculated based on the mass flow. Electric energy consumption at EED or EC was calculated for multiplying required current and voltage at the apparatus. Electric energy was assumed to be obtained at the rate of 40 % from the heat source. The waste heat was not recovered as electricity. The major assumptions for the calculation were listed in the Table 1. Total thermal efficiency ($\eta$ [%]) was defined as follows. Higher heat value of H_2 is divided by sum of heat demands from heat source (H_{heat}) and heat demands for electricity (H_{elec}).
In this report, effects of three kinds of membrane techniques on the IS process were investigated.

1. HPMR at HI decomposition reaction (No. 3 in Figure 1): Parameters, HI conversion
2. EED at HI concentration procedure (No. 2 in Figure 1): Parameters, HI concentrations after EED
3. EC at liquid-liquid separator and HI concentration procedure (No. 1 and 2 in Figure 1): Parameters, HI concentration, I₂ concentration, H₂SO₄ concentration.

First, Effects of HI conversion by HPMR were discussed, because HPMR is independent of EED or EC results. Next, differences of EED and EC were investigated under the same calculation conditions. EED is just a concentrator of HI after the liquid-liquid separation of HI solutions and H₂SO₄ solutions, while EC is a combination of the separator and the concentrator.

RESULTS AND DISCUSSIONS

Hydrogen permselective membrane reactor (HPMR)

Figure 3 shows the total thermal efficiency plotted as a function of HI decomposition conversion. Thermal efficiency was increased with increasing HI conversion. The amount of required heat to increase the temperature

\[ \eta = \frac{\Delta H_{H_2,HIe} \left( = 285.8 \text{kJmol}^{-1} \right)}{H_{\text{heat}} + H_{\text{elec.}}} \times 100 \]
of HI vapor before the membrane reactor from HI, I₂ and hydrogen mixtures can be applied when HI conversion is over 50%. No heat demands are needed from the other part of the processes, and thermal efficiency was increased from ca. 50% of the HI conversion. However, thermal efficiency difference was only 1% by changing HI conversions showing that HPMP is not the best choice to improve thermal efficiency. HPMR should be applied to decrease H₂ partial pressure for the stability of metallic vessels or pipes under HI, H₂O and H₂ atmosphere after the HI decomposer.

**Electro-electrodialysis (EED)**

Figure 4 shows the relation of thermal efficiency and HI concentration after EED at 0 V of overpotential at EED. The maximum thermal efficiency (40.8%) was found at 12.5 mol kg⁻¹ H₂O⁻¹ of HI concentration after EED. Electric energy consumption at EED is increased with increasing HI concentration after EED, because cell voltage is decided by the concentration (activity) difference of HI at the cell. At lower concentrations than 12.5 mol kg⁻¹ H₂O⁻¹, it is better to concentrate HI at EED by using electric power. While electric energy consumption was too much at higher than 12.5 mol kg⁻¹ H₂O⁻¹, and it is better to concentrate HI at HI distillation column using heat. Thermal efficiency was changed by more than 30% by changing HI concentration after EED. This parameter is very important for the evaluation. This must be because amounts of recycling chemicals at the bottom of the HI distillation column was huge when EED was applied to the IS process. 347 mol s⁻¹ of HI, I₂ and H₂O was recycled at the bottom of the HI distillation column for 1 mol s⁻¹ of H₂. This method is effective by heat/mass balance evaluation. The energy demand for pumping has to be evaluated for this method.

**Electrochemical cell (EC)**

Effects of I₂ concentrations in the catholyte were investigated. Figure 5 shows current densities and total cell voltages by changing I₂/HI ratios in the catholyte. The cell voltage was proportional to current density. HI concentration and H₂SO₄ concentration were fixed at 10.0 mol kg⁻¹ H₂O⁻¹ and 13.0 mol kg⁻¹ H₂O⁻¹, respectively. It is obvious that the total cell voltages are independent of I₂ concentration in catholyte. This shows that I₂ concentrations under the experimental conditions have little effect on I₂ activity and solution resistances. I₂/HI ratio can be decreased till 0.5 not to change any electrochemical properties. This is only 12.5% of I₂ amounts that should be treated at EED discussed in the former section. I₂/HI ratio was
fixed at 1 in the following discussions. The cell voltage at zero of current was defined as $V_0$ [V], and the slope of the plots was also defined as ER (electric resistance of the cell) [$\Omega$ dm$^2$]. $V_0$ is the minimum required voltage for the experimental conditions. In order to operate EC efficiently for the thermal efficiency of the IS process, this cell should operate at lower current density. However, the required membrane area increased with decreasing current density of the cell. The balance of the current density and the cell voltage should be discussed. In this section, $V_0$ was optimized for the efficient operation primary, and effects of $V_0$ and ER was discussed later. Figure 6 shows $V_0$ by changing HI or H$_2$SO$_4$ concentration. For circle plots, H$_2$SO$_4$ concentration in anolyte was fixed at 12.4 mol kg$^{-1}$H$_2$O, and only HI concentration in catholyte was changed. HI concentrations have little effects on $V_0$ under the operating conditions, while $V_0$ for H$_2$SO$_4$ increased increasing with H$_2$SO$_4$ concentrations. $V_0$ is related to chemical potentials (activity) of the reactants at the both side of the electrodes. Usually, activity is increased with increasing the concentration of chemicals. HI concentration might be too high for activity change by the concentration differences. For H$_2$SO$_4$ concentrations, SO$_2$ activity might be decreased in extremely high H$_2$SO$_4$ solutions, and $V_0$ increased by the H$_2$SO$_4$ concentration change. On the other hand, trend of ER for both HI and H$_2$SO$_4$ shown in Figure 7 look similar. Electric resistance of the cell increased with increasing HI or H$_2$SO$_4$ concentrations. One possible explanation is dehydration of the cation exchange membrane in the high acids conditions. Further investigation is required to reduce electric resistance at higher HI or H$_2$SO$_4$ concentrations.
In order to evaluate the electric energy consumption and concentration of both acids, heat/mass balance of the total process was calculated. Figure 4 shows total thermal efficiency by changing HI concentration at EC using $V_0$ for the cell voltage. $\text{H}_2\text{SO}_4$ concentration was fixed at 12.4 mol kg$^{-1}\text{H}_2\text{O}$. $V_0$ was slightly increased by HI concentration shown in Figure 6. Electric energy consumption is almost the same by concentration of HI at the EC. Thermal efficiency was increased with increasing HI concentration after the EC. HI concentration should be higher in the range of 10.8 – 16.7 mol kg$^{-1}\text{H}_2\text{O}$. Figure 9 shows total thermal efficiency and $\text{H}_2\text{SO}_4$ concentration after the EC. The maximum thermal efficiency of 38.9 % was obtained at 15.3 mol kg$^{-1}\text{H}_2\text{O}$ of $\text{H}_2\text{SO}_4$ concentration. At lower $\text{H}_2\text{SO}_4$ concentration, $\text{H}_2\text{SO}_4$ is better to be concentrated by using electricity at EC. At higher $\text{H}_2\text{SO}_4$ concentration, $\text{H}_2\text{SO}_4$ should be concentrated by using heat at the evaporator. Table 2 shows the lists of each heat demand for the calculation results at HI = 11.8 mol kg$^{-1}\text{H}_2\text{O}$. Electric energy at EC was calculated based on $V_0$, and this value was divided by 0.40 on the assumption that power generation efficiency is 40%. Heat demand to produce electric energy at 16.7 mol kg$^{-1}\text{H}_2\text{O}$ of $\text{H}_2\text{SO}_4$ was ca. 50 kJ mol$^{-1}$ larger than that at 10.2 mol kg$^{-1}\text{H}_2\text{O}$. On the other hand, heat demand to vaporize $\text{H}_2\text{SO}_4$ was decreased by the concentration of $\text{H}_2\text{SO}_4$ at EC. The reduction of heat demand at $\text{H}_2\text{SO}_4$ system was more than 100 kJ mol$^{-1}$. In this case, the maximum thermal efficiency for the EED was indicated in Figure 8 under the similar operating

<table>
<thead>
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<th>Table 2 Breakdown lists of the calculation results shown in Figure 8</th>
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<td><strong>Unit</strong></td>
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<tr>
<td><strong>H$_2$SO$_4$ conc.</strong>  mol kg$^{-1}\text{H}_2\text{O}$</td>
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<td>Electric energy at EC  kJ mol$^{-1}$</td>
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<td>Heat for electric energy: $H_{elec}$  kJ mol$^{-1}$</td>
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<td>Heat demand at $H_2SO_4$ system  kJ mol$^{-1}$</td>
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<td>Heat demand at HI system  kJ mol$^{-1}$</td>
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<td>Heat demand: $H_{heat}$  kJ mol$^{-1}$</td>
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<td>Total heat demand: $H_{heat}+H_{elec}$  kJ mol$^{-1}$</td>
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<td>Thermal efficiency  %</td>
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HI conc. 11.8 mol kg$^{-1}\text{H}_2\text{O}$
conditions. The maximum thermal efficiency for EED was slightly higher than that for EC. However, EC has merits for EED by the simple process configuration and small amounts of recycling chemicals. Total initial cost can be reduced for 20% by the application of the EC to the IS process (Nomura et al. 2003). In order to replace EC instead of EED, $H_{\text{elec}}$ shown in table 2 should be reduced by about 30%. Figure 9 shows the result of the calculations. As shown in Figure 7, ER of the EC was increased with increasing $H_2SO_4$ concentrations. The slopes of the calculation lines were sharp for the higher $H_2SO_4$ concentrations. All the thermal efficiencies were similar values at 3 A dm$^{-2}$ of the current density. It is better to use lower $H_2SO_4$ concentrations at 10 A dm$^{-2}$ of the current density. However, the efficiency decreased with ca. 10% at 10 A dm$^{-2}$ of the current density from the values at $V_0$. Thus, total resistances should be improved by the developments of membrane or electrodes.

CONCLUSIONS

The three membrane techniques proposed to improve the IS process were investigated by total thermal efficiency to produce hydrogen. The thermal efficiency through the IS process was evaluated by calculating total heat/mass balance of both $H_2SO_4$ system and HI system. Application of a hydrogen permselective membrane to HI decomposition reaction is not effective for the point to improve the total thermal efficiency. Only 1% of the thermal efficiency can be improved from that of the equilibrium conversion. This technique should be employed to avoid hydrogen embrittlement under HI, $H_2O$ and $H_2$ at the recycling procedures after HI decomposition reaction. The second membrane technologies discussed in this report was application of electro-electrodialysis (EED) to concentrate HI after the Bunsen reaction. Thermal efficiency showed the highest values among three techniques. However, thermal efficiency seems to be too sensitive to control the total process by the huge amounts of recycling $I_2$ and $H_2O$ after the EED. The final one is the electrochemical cell (EC) for the Bunsen reaction of the IS process. The maximum thermal efficiency was slightly smaller than that for EED. However, this technique has a potential to improve the total process by simplify the total process and by reducing the recycling chemicals such as $I_2$. In order to apply the EC instead of the EED, required electric energy demand for the EC should be reduced by ca. 30% by improving membrane resistances or the losses at the electrodes.
REFERENCES


