Development of an Electrochemical Cell for Efficient Hydrogen Production through the IS Process

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The Bunsen reaction ($SO_2 + I_2 + 2H_2O = H_2SO_4 + 2HI$) was examined by an electrochemical cell featuring a cation-exchange membrane as the separator, using sulfuric acid dissolving sulfur dioxide as the anolyte and hydriodic acid dissolving iodine as the catholyte. In galvanostatic electrolysis, the molality of H_2SO_4 in the anolyte and that of HI in the catholyte were increased up to 17.8 and 14.9 mol kg_{H2O}^{-1}, respectively. These concentrations were far higher than those that were obtained by the Bunsen reaction carried out in the presence of a large amount of iodine (such as $I_2/HI = 4$). I_2 concentration after the concentration procedure was at $I_2/HI = 0.95$, which is lower than the reported value. I_2 is one of the recycling agents in the IS process. HI and H_2SO_4 were successfully concentrated under low I_2 concentration. The concentration of HI agreed with the calculated value, based on the amount of electricity consumed, indicating high current efficiency. Heat/mass balance using this type of electrochemical cell through the IS process is discussed for evaluation of the reactor. The thermal efficiency to produce hydrogen was calculated at 42.1%, without heat recovery for electricity, by optimizing HI and H_2SO_4 concentrations after application of the electrochemical cell. © 2004 American Institute of Chemical Engineers *AIChE J,* 50: 1991–1998, 2004

Keywords: hydrogen production, IS process, Bunsen reaction, electrochemical cell, cation-exchange membrane

Introduction

A water-splitting method using nuclear heat is a promising method for stable hydrogen production without CO_2 emission. Hydrogen can be obtained from water at temperatures lower than direct water decomposition temperatures (~4000 K) using certain chemicals as catalysts. Typical thermochemical water-splitting methods are the UT-3 (for example, Aihara et al., 1992; Kameyama et al., 1978; Sakurai et al., 1992, 1995) and the iodine–sulfur (IS, or SI) (for example, Norman et al., 1981) processes. The UT-3 process consists of four chemical reactions using Ca, Br, and Fe (Kameyama et al., 1978). All the chemicals used in the cycle are either solid or gas phase. The one-loop flow scheme was demonstrated by switching the gas

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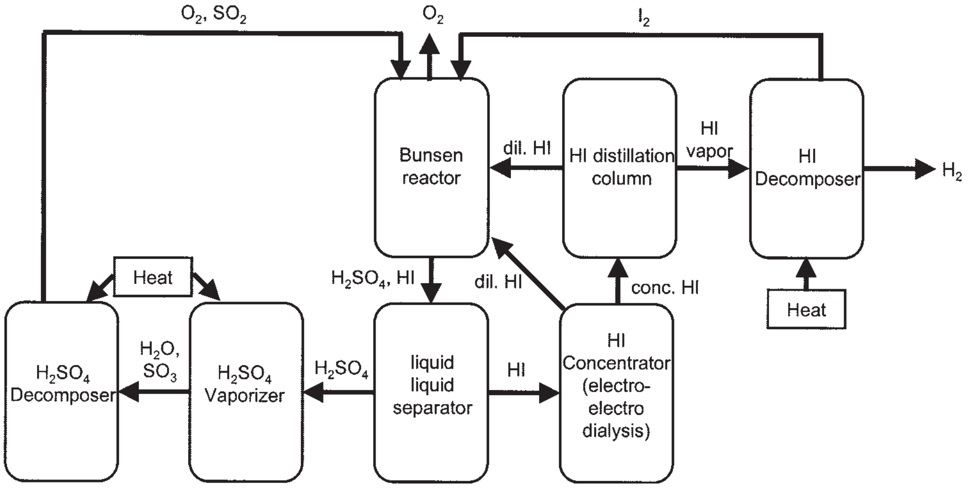


Figure 1. Simple process diagram of the IS process.

flows (Sakurai et al., 1992). On the other hand, the major chemicals are liquid or gas phase for the iodine-sulfur (IS) process, which was originally developed by the research group of General Atomic (GA) (Norman et al., 1981, 1982). The IS process mainly consists of three reactions, described as follows:

(1) $SO_2 + I_2 + 2H_2O = H_2SO_4 + 2HI$ (~400 K, the Bunsen reaction)

(2) $H_2SO_4 = H_2O + SO_2 + 0.5O_2$ (700–1200 K)

(3) $2HI = I_2 + H_2$ (500–800 K)

HI and H_2SO_4 are produced during the Bunsen reaction as intermediate products. These acids are decomposed using high-temperature heat around 500–1200 K. H_2 and O_2 are obtained as products by the decomposition of acids, and I_2 and SO_2 are recycled to the Bunsen reaction. H_2O is decomposed into H_2 and O_2 through the chemical reactions.

Japan Atomic Energy Research Institute has been actively developing the IS process (for example, Kubo et al., 2001; Onuki et al., 1994). Continuous hydrogen production at the rate of 1 L_{H2}/h was demonstrated using the glass-made apparatus (Nakajima et al., 1998, 1999). However, the thermal efficiency required to produce hydrogen was poor because too much steam and other chemicals were recycled in the process. Efficient operation is necessary to actualize the IS process. There are three major useless recycling agents in the IS process. (1) H_2O after an HI distillation procedure. The azeotropic composition of HI solution is low, and great amounts of steam were introduced into a decomposition reactor. For example, the azeotropic concentration of HI is 11.0 mol kg_{H2O}^{-1} (11.2 mol %) when the I_2 concentration is 31.5 mol kg_{H2O}^{-1}. (2) HI vapor after the decomposition reactor, given that the equilibrium decomposition rate of HI was about 20%. (3) I_2 between the Bunsen reaction and an HI distillation column. An excess amount of I_2 was added to stabilize and separate the HI solution at the Bunsen reaction. The optimum compositions after a liquid–liquid separator were reported to be ($H_2SO_4 + 4.1H_2O$) and ($2HI + 7.6I_2 + 10.6H_2O$) (Norman et al., 1982). I_2 (7.6 mol) and H_2O (14.7 mol) were added to separate HI and H_2SO_4 for 1 mol of product H_2.

Figure 1 shows the simple process diagram of the IS process using an electro-electrodialysis (EED) method for concentration of HI solution after the Bunsen reaction. This method is effective in reducing the recycling of H_2O after the distillation procedure (Arifal et al., 2002; Onuki et al., 2001). The steam obtained at the top of an HI distillation column can be reduced by concentrating HI over the pseudo-azeotropic compositions of the HI–I_2–H_2O system before the distillation. The GA group (Norman et al., 1982) proposed the use of H_3PO_4 for the concentration of HI solution. A high concentration of HI vapor (99.7 mol %) was obtained by adding H_3PO_4 to HI solutions. The remaining H_3PO_4 solution was concentrated by using heat and electricity. These are techniques for the reduction of the first major recycling agent (H_2O) described above. An H_2 permselective membrane reactor was examined to improve the conversion ratio of HI decomposition reaction (Hwang et al., 2000, 2001). Recycled HI vapor (second major recycling agent) can be decreased by improvements of a one-pass conversion of HI. The effects of an EED and an H_2 permselective membrane reactor were evaluated in terms of the total thermal efficiency to produce hydrogen through the IS process (Kasahara et al., 2003; Nomura et al., 2003a). EED should be operated very carefully because the HI concentration after an EED cell has a considerable effect on the total thermal efficiency, which shows that the mass around the HI concentration procedure was substantial. The amount of I_2 after the Bunsen reaction is the key to efficient operation. More than 1900 g (7.6 mol) of I_2 was recycled to produce 2 g (1 mol) of H_2, based on the traditional liquid–liquid separator. HI and I_2 form a complex in water solution. Densities of the complex are increased with increasing I_2 concentration. To separate HI from H_2SO_4 solution using liquid–liquid separator, at least 7.6 mol of I_2 is required for 1 mol of product H_2. The concentration of HI should be lower than that of I_2.

Recently, a new approach using an electrochemical cell was proposed to reduce the amount of I_2 after the Bunsen reaction (Nomura et al., 2003b). Figure 2 shows the process diagram using an electrochemical cell in the Bunsen reaction. HI separation and decomposition procedures are integrated into this Bunsen reactor. The idea of applying this type of electrochemical cell to the Bunsen reaction was previously reported by Dokiya et al. (1977), although effects of reducing I_2 using the cell were not investigated. Figure 3 shows the reactor. A

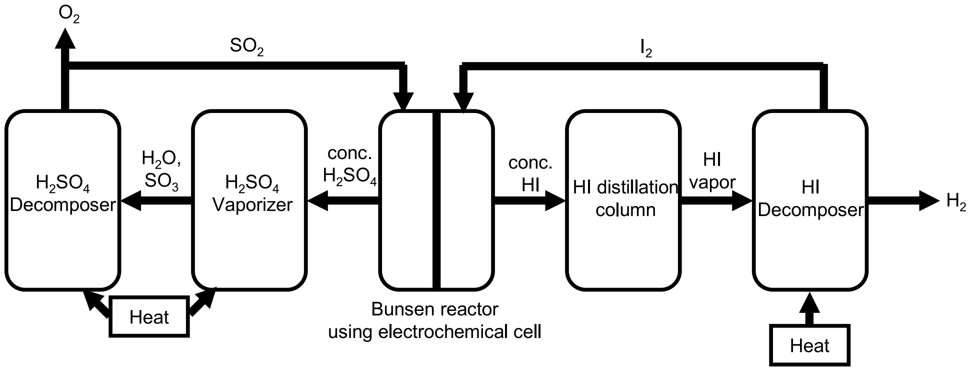


Figure 2. Simple process diagram of the IS process using electrochemical cell for the Bunsen reaction.

solution of HI and I_2 is supplied at the cathode side, and a solution of SO_2 is supplied at the anode side. The electrode reactions are described as follows

Anode reaction: $SO_2 + 2H_2O = H_2SO_4 + 2H^+ + 2e^-$
Cathode reaction: $I_2 + 2H^+ + 2e^- = 2HI$
Total reaction: $SO_2 + 2H_2O + I_2 = H_2SO_4 + 2HI$ (the Bunsen reaction)

The H_2SO_4 solution and the HI solution are obtained separately at both sides of the cation-exchange membrane. There are three advantages of applying this method: (1) to reduce recycling I_2 by omitting a liquid–liquid separator, and thus I_2 was added to increase density of HI solution for a liquid–liquid separator; (2) increase simultaneously the concentration of HI and H_2SO_4, and thus recycling H_2O can be reduced; (3) to simplify the system by coupling a Bunsen reactor and an HI–H_2SO_4 separator and HI concentrator (compare Figures 1 and 2). This electrochemical cell was successfully demonstrated at room temperature using 3.1 mol kg_{H2O}^{-1} of HI solution. Ninety-three percent of an excess amount of I_2 was reduced by using this reactor (Nomura et al., 2004). Cost evaluation was also conducted for the application of this type of electrochemical cell. Total hydrogen cost was reduced by 23% by decreasing 93% of I_2 at the Bunsen reaction (Nomura et al., 2003b). The concept of the application of the electrochemical cell is promising. However, concentrations of HI and H_2SO_4 should be higher for efficient operations. In this article, HI and H_2SO_4 were concentrated to values higher than those obtained by the liquid–liquid separator. The concentrations of HI, I_2, and H_2SO_4 from the liquid–liquid separator were 10.5, 39.8, and 13.5 mol kg_{H2O}^{-1}, respectively (Norman et al., 1982). Thus, the target concentrations of HI and H_2SO_4 were greater than 10.5 and 13.5 mol kg_{H2O}^{-1}, and the I_2/HI ratio was less than 3.8 mol mol^{-1}. Because HI and H_2SO_4 are intermediate products, and I_2 is recycling agent, especially for HI concentration, it is important that the concentrate be greater than the pseudo-azeotropic concentration. The pseudo-azeotropic concentration of HI solution is about 10 mol kg_{H2O}^{-1}. The experimental results were also evaluated by the total thermal efficiency to produce hydrogen based on heat/mass balance calculation.

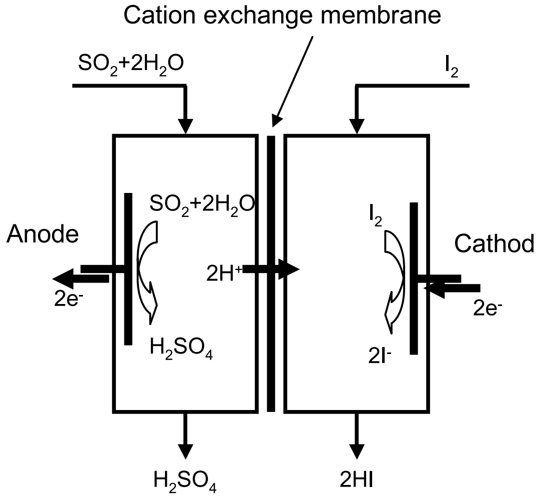


Figure 3. Schematic diagram of an electrochemical cell.

Experimental

The experiment was carried out at 290–333 K under a constant current. Temperature of the module was controlled using heaters at both sides of the electrodes. A temperature sensor was set at the outlet of the HI solution. Nafion 117 (Dupont) was used as a cation-exchange membrane, and a carbon felt provided by Toyobo was used for the electrodes. The effective membrane area was 5.06×10^{-4} m^2. HI solution, H_2SO_4, and I_2 were provided by Kanto Chemical Co. HI and H_2SO_4 solutions were diluted to the specified concentration using deionized water and poured into 200- or 400-mL flasks. The solutions were circulated to the electrochemical cell by using the roller pump (RP-100, Tokyo Rikakiki Co.). Pure SO_2 gas, supplied by Sumitomo Seika Co., was introduced into the H_2SO_4 solution by bubbling at the rate of 20 mL min^{-1} during the experiment. The concentration of each component was measured by titration using Comtite COM-900 (Hiranuma Co.). KIO_3 (0.02 M), $Na_2S_2O_3$ (0.1 N), and NaOH (0.1 N) were used for the titration. KIO_3 was used to measure I^- and Na_2S2O_3 was used for I_2 titration. The total amount of H^+ was measured by using NaOH. Titration procedures were continued until errors of the titration procedures were $<1\%$. The current was controlled by an HA-305 potentiostat/galvanostat (Hokuto Denko). Details of the experimental procedures are described in the literature (Nomura et al., 2004).

Table 1. Electrochemical Cell Reaction Results after 4-h Operation at Room Temperature

Run	Composition	Initial Concentration (mol kg_{H2O}^{-1})	Final Concentration (mol kg_{H2O}^{-1})	Calculated Concentration (mol kg_{H2O}^{-1})	H_2O (g)	ΔV (V)
1	HI	3.03	3.63	3.50	−1.58	−0.009
	I_2	0.43	0.18	0.19		
	H_2SO_4	3.78	4.09	3.99	−4.60	
2	HI	10.1	9.55	10.7	5.38	−0.041
	I_2	1.38	1.22	1.09		
	H_2SO_4	3.82	4.34	4.05	−8.69	
3	HI	10.2	9.80	10.8	4.75	0.175
	I_2	10.3	9.52	10.0		
	H_2SO_4	3.82	4.28	4.03	−9.87	
4	HI	10.2	10.7	10.8	−0.59	0.247
	I_2	10.1	9.86	9.77		
	H_2SO_4	13.7	14.7	14.1	−3.76	

Results and Discussion

Effects of HI and H_2SO_4 concentrations

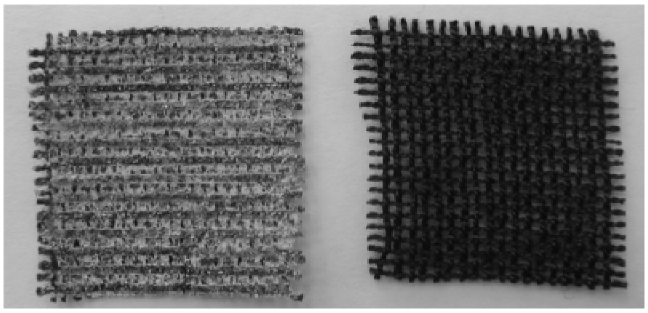
Effects of HI or H_2SO_4 concentrations were investigated for the 4-h operation under 0.3 A at room temperature. Table 1 shows the initial and final concentrations with the calculated concentrations, H_2O amounts, and ΔV. Initial HI, I_2, or H_2SO_4 concentrations were varied to compare the effects of acid compositions. The third column from the left shows the initial concentrations of the experiment. HI and I_2 indicate the concentrations of the catholyte and H_2SO_4 shows the concentrations of the anolyte. The fourth column from the left shows the final concentrations after 4-h operation at 0.3 A. These concentrations were measured by titration. The fifth column shows the equivalent concentrations calculated from the initial concentrations and the quantities of electricity (4 h × 3600 s × 0.3 A = 4320 C). The sixth column indicates the change of H_2O amounts during the operation for both the anolyte and the catholyte. There were some errors (a few grams) in weighing after the operation. Small amounts of solutions remained in the reactor. The total amounts of H_2O were less than the initial amounts. The seventh column from the left shows the voltage differences at 0 electric current, indicating the electromotive force at the HI and H_2SO_4 concentrations. These values were evaluated from the current–voltage figure by using an extrapolating method.

Run 1 shows the result for low concentrations of HI and H_2SO_4. The concentration procedure of HI and H_2SO_4 was successfully carried out within 4% of error from the calculated concentrations under low I_2/HI ratio (0.14). Next, the initial HI concentration was increased to 10.12 mol $kg_{H2O}{}^{-1}$, but keeping the I_2/HI ratio (Run 2). The final HI concentration was decreased to 9.55 mol $kg_{H2O}{}^{-1}$ after the operation. Figure 4 shows the photograph of the cathode electrode after the experiment. The electrode was white compared with the fresh carbon electrode. H_2S and SO_2 were detected at the catholyte. These white particles at the electrode were sulfur reduced from SO_2 in the catholyte. The chemical reactions might be "$SO_2 + 4HI = S + 2H_2O + 2I_2$". Permeated SO_2 from the anolyte reacted with HI in the catholyte, and the HI concentration was deceased after the operation. The amounts of H_2O in the catholyte were increased for Run 2, which indicates that H_2O passed though the membrane (compare Run 1). The dissolved SO_2 in the anolyte passed through the membrane along with H_2O.

The concentration of I_2 was increased to stabilize catholyte for Run 3. The I_2/HI ratio was 1.0 for the initial concentrations. The presence of I_2 in the HI solution stabilized the solution from SO_2 reduction reactions (Sakurai et al., 2000). The final HI concentration, however, was lower than that of the initial concentration. Sulfur was found at the cathode electrode. Amounts of H_2O in the catholyte were also increased after the operation. The I_2 concentration was not sufficient to stabilize the solution for Run 3.

H_2SO_4 concentration was increased to 13.7 mol $kg_{H2O}{}^{-1}$ for Run 4. HI was concentrated from 10.2 to 10.7 mol $kg_{H2O}{}^{-1}$, which is higher than the pseudo-azeotropic concentration of HI (10.0 mol $kg_{H2O}{}^{-1}$) for this I_2 concentration. The error from the calculated concentration was about 1.3%, indicating that the side reaction of sulfur was not a major reaction. The amount of H_2O in the HI solution was not increased after the operation. The amount of H_2O that passed through the membrane from anolyte to catholyte was obviously smaller than that for either Run 2 or Run 3. Osmosis pressure of the anolyte is higher for Run 4. H_2SO_4 concentration should be higher to ensure a stable operation.

ΔV shows the activity difference of SO_2, H_2SO_4, HI, and I_2, given that the electrode reactions are the same (anode: $SO_2 + 2H_2O = H_2SO_4 + 2H^+ + 2e^-$, cathode: $I_2 + 2H^+ + 2e^- = 2HI$) for Runs 1–4. The concentration of HI has a negligible influence on ΔV, in a comparison of Runs 1 and 2, whereas ΔV increased by 0.216 V by increasing I_2 concentration in the catholyte (Runs 2 and 3). If the I_2 activity at the cathode increases with increasing I_2 concentration, ΔV decreases for Run 3. There should be resistance effects by varying the I_2 concentration. Further investigations are required to determine



Cathode electrode after Run No.2 in Table 1

Fresh electrode for comparison

Figure 4. Photographs of carbon electrode.

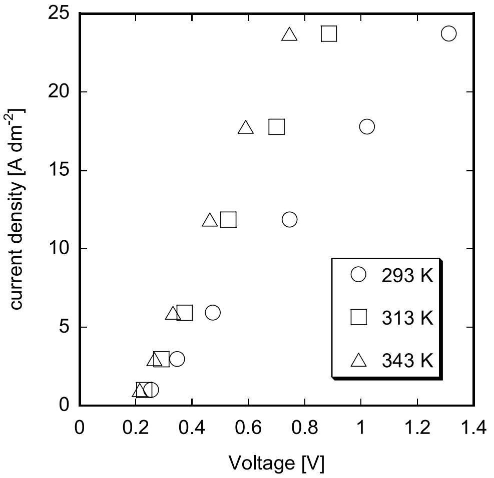


Figure 5. Effects of operating temperature on total voltage.

the effect of I_2 concentrations on ΔV. In a comparison of Runs 3 and 4, it is obvious that ΔV increased with increasing H_2SO_4 concentration in the anolyte, which can explain the H_2SO_4 activity difference for Runs 3 and 4.

The final concentrations of HI and H_2SO_4 of Run 4 were higher than those from a liquid–liquid separator (Norman et al., 1982). However, electric power is required for this procedure. At least 0.074 W (0.30 A × 0.247 V) is required for this reactor. The balance of required electric energy and concentrations of acids are discussed in a later section.

Effects of operation temperature on total voltage

The total voltage between the electrodes for EED of $HI–I_2–H_2O$ solution sharply decreased by elevating the cell temperature (Onuki et al., 2001). In this case, the $HI–I_2–H_2O$ solution was introduced to both sides of a cation-exchange membrane. Onuki and coworkers concluded that membrane resistances decreased with increasing operation temperature, especially for high HI concentrations. The operating temperatures were increased up to 333 K for this electrochemical cell. Figure 5 shows the current density of the electrochemical cell, plotted as a function of total voltage, by varying the operating temperatures. HI and H_2SO_4 concentrations were 10.2 and 13.7 mol kg_{H2O}^{-1}, respectively, and the I_2/HI ratio was fixed at 1. Current densities and total voltages were proportional for each operating temperature. The slope indicates the total resistance between the electrodes and the x-intercept (ΔV) indicates the potential difference. The resistances between the electrodes decreased with increasing operating temperatures, in a trend similar to that of the EED of the $HI–I_2–H_2O$ system. The membrane resistance was reduced by increasing the operating temperature. Total resistance at 343 K was about 60% from that at room temperature. Electric energy at the reactor is effectively reduced by increasing operation temperatures. In contrast with the resistance, the x-intercepts were similar for all temperatures, indicating that the activity at both sides of the membrane was not significantly different as a result of temperature change.

Continuous concentration of HI and H_2SO_4

HI was concentrated over the pseudo-azeotropic composition of $HI–I_2–H_2O$ systems for 10-h operation at 313 K. Current was maintained at either 1.2 or 0.6 A, but was decreased from 1.2 to 0.6 A at 5 h to avoid side reactions. The anode-side electrode (carbon) could react with H_2O into CO or CO_2 over 3 V of the total voltage. Figure 6 shows the time course of HI and I_2 concentrations. Initial concentrations of HI and I_2 were 9.77 and 15.0 mol kg_{H2O}^{-1}, respectively; HI concentration was increased with operation time. The final concentration was 14.9 mol kg_{H2O}^{-1}, which is much higher than the pseudo-azeotropic concentration. The final HI concentration agrees with the calculated value, shown in the figure as a calculated line within 1.4% of error. This indicates that the side reactions were not significant during the operation. There was no sulfur found at the cathode-side electrode after the experiment. Electricity was consumed very efficiently for the electrode reactions. I_2 concentration decreased during the reaction, and the final concentration was 14.1 mol kg_{H2O}^{-1}. As a result, the final I_2/HI ratio was 0.95. These HI concentrations and I_2/HI ratios were superior to the target values shown earlier in the introductory section.

H_2SO_4 was concentrated from 12.5 to 17.8 mol kg_{H2O}^{-1} by the operation. The final molar ratio of H_2SO_4 and H_2O was 3.1. About 1 mol of recycling H_2O can be reduced for 1 mol of H_2SO_4 by the decomposition procedure compared with the traditional liquid–liquid separation method. A small amount of HI (0.12 mol kg_{H2O}^{-1}) was detected in the anolyte. I^- was passed through the cation-exchange membrane. The apparent transform number of this membrane was 0.98, calculated by the amounts of HI in the anolyte and the total electricity used during the operation. The leakage of I^- from the catholyte is not a major problem for this system. HI can be easily removed from the solution by a reverse Bunsen reaction, and 3 ppm of HI in the anolyte reduces the total voltage by 0.03 V (Nomura et al., 2004).

HI, I_2, and H_2SO_4 concentrations were much better than the target values. A discussion of the electricity consumption for the reactions would be helpful at this point. The current was

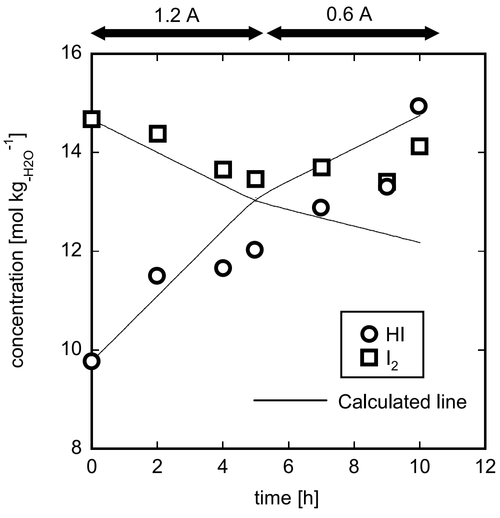


Figure 6. Continuous concentration by the electrochemical cell.

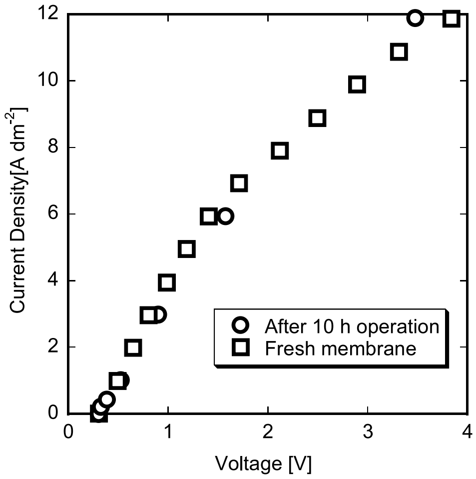


Figure 7. Current density plotted as a function of total voltage for the final concentrations.

increased with increasing operation time as a consequence of membrane resistance; solution resistance; and activity difference of the reaction, which is discussed first. The circle plots in Figure 7 show the current density and total voltage at the final solutions of Figure 6. Current density was almost proportional to total voltage. ΔV (*x*-intercept) and total resistance were 0.28 V and 0.22 Ω dm^2, as observed from the figure. ΔV was slightly increased over the value shown in Figure 5 at 313 K (0.19 V). This difference (0.09 V) shows the activity difference by the concentration of HI and H_2SO_4. The electromotive force, by the activity difference at the catholyte, was calculated by assuming that the activity of I_2 was 1. The electromotive force difference, by the difference in HI concentration for the initial and final HI concentrations, is 0.07 V, which is similar to the ΔV difference. The main reason for the ΔV difference shown in Figures 5 and 7 was the HI concentration difference in the catholyte. On the other hand, the total resistance increased more than sevenfold over that shown in Figure 5 (2.9×10^{-2} Ω dm^2). This resistance consists of both solution resistance and membrane resistance.

The cation-exchange membrane after the experiment appeared white. This shows that a small amount of sulfur was deposited on the membrane. Thus, the total resistance was measured using a fresh cation-exchange membrane at the same solution concentrations. The results are also plotted in Figure 7 as square symbols. The square symbols and the circle symbols look similar, indicating that the membrane resistance was not affected by the 10-h operation. Figure 8 shows the relation between current density and total voltage at 313 K by changing the anolyte concentrations. HI concentration in the catholyte was fixed at 16.7 mol kg_{H2O}^{-1} under I_2/HI = 1. The *x*-intercepts look similar for all H_2SO_4 concentrations, which shows that activity is only slightly influenced by H_2SO_4 concentration at 16.7 mol kg_{H2O}^{-1} of HI concentration, whereas the slopes varied according to the H_2SO_4 concentrations, indicating that the solution resistance of H_2SO_4 increases with increasing concentration. The slope was not significantly changed by the HI concentration in the catholyte. The higher resistance at higher H_2SO_4 concentration can be explained by the solution resistance of H_2SO_4 concentration difference or dehydration of the Nafion membrane at higher H_2SO_4 concentration.

Evaluation based on heat/mass balance calculations

HI and H_2SO_4 were successfully concentrated under low I_2/HI ratio (0.95), as reported in the previous section. This method, however, consumes electric energy for the reaction. The effects of concentrations of acids and reduction of I_2 should be evaluated by the total energy consumption to produce hydrogen based on the heat/mass balance. For comparison with the proposed system, a basic hydrogen production system for the IS system was assumed, as shown in Figure 1. Heat/mass balance was calculated under steady state. A multieffect evaporator (Knoche et al., 1984) was used for vaporization and decomposition of the H_2SO_4 system. An EED method and a hydrogen permselective membrane reactor were used for concentration and decomposition of HI. The current in the EED cell was calculated by the mass balance of the process. Pressure of the HI distillation was fixed at 9.8×10^5 Pa, and the reflux ratio was set at 0.5 for the calculations. The production rate of hydrogen was set at 1 mol s^{-1}. The compositions after the Bunsen reaction were (H_2SO_4 + 4.1H_2O) and (2HI + 7.6I_2 + 10.6H_2O). The temperature difference at the heat exchangers was fixed at 10 K. Waste heat was recovered as heat and was not recovered as electricity. Generation efficiency of electricity from the heat source was assumed at 40%. The detailed assumptions and the calculation procedures are described elsewhere (Kasahara et al., 2003).

First, thermal efficiency was calculated using an EED method for the concentration of HI. Next, an electrochemical cell system was applied instead of an EED method, as shown in Figure 2. The process consists of four parts: (1) The Bunsen reaction segment, using the electrochemical cell for the reaction. H_2SO_4 solutions and HI solutions were obtained separately through the cell. (2) A solution of H_2SO_4 was introduced into a multieffect evaporator (not shown in the figure) to decompose into O_2 and SO_2. (3) The HI distillation segment, which is composed of only a distillation column and heat exchangers without EED (this is the difference between this system and the basic system). (4) HI decomposition /separation segment, where H_2 is obtained as a product. The heat/mass balance was calculated using the same assumptions as the basic

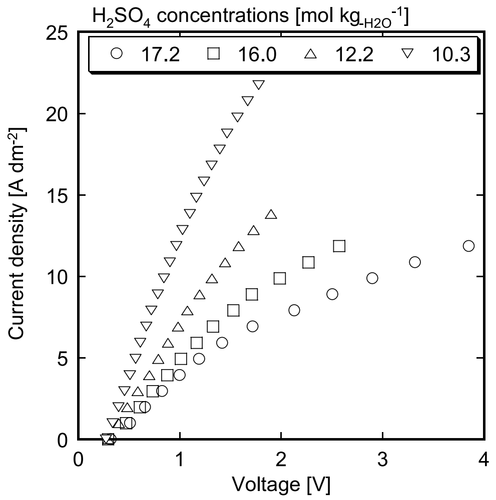


Figure 8. Current density and total voltage by changing anolyte concentration at 313 K.

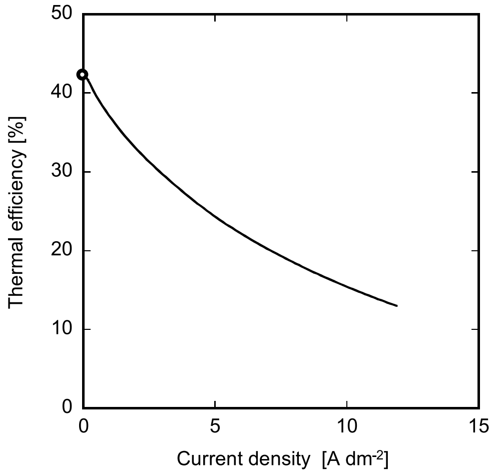


Figure 9. Effects of current density on thermal efficiency.

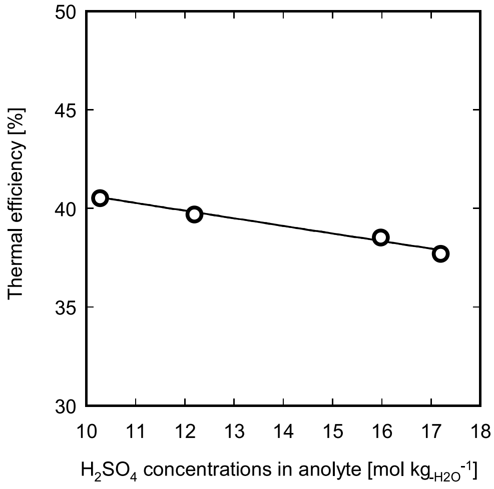


Figure 10. Effects of H_2SO_4 concentrations on total thermal efficiency.

hydrogen production system. H_2SO_4 concentrations for the electrochemical cell were higher than that for the assumption described above. The difference in concentration was compensated by dilution heat of H_2SO_4 solution from the total electricity demands.

Figure 9 shows the relation between thermal efficiency to produce hydrogen and current density of the cell. The detailed electricity and heat demands for Figure 9 are shown in Table 2. Values for current density and total voltage were used from the experimental values shown in Figure 7. The electricity consumptions were calculated by the currents and the total voltages at the cell. Required electricity was the sum of recovery at H_2SO_4 concentration part and consumption at the electrochemical cell. "Recovery at H_2SO_4 concentration system" in Table 2 represents electric power generated from heat recovered during cooling of H_2O and SO_2 from the decomposition of H_2SO_4. Heat demand for electricity was calculated by dividing "Electricity required from outside of the system" by 0.40. Thermal efficiency to produce hydrogen was the ratio of high heat value of H_2 and the total heat demand; the maximum thermal efficiency was 42.3%. However, thermal efficiency decreased sharply with increasing current density of the electrochemical cell. Heat demand for electricity increased by 1526.9 kJ $mol_{H2}{}^{-1}$ by increasing current density to 11.9 A dm^{-2}. As a result, the thermal efficiency was only 13.0%. The electric loss by the solution resistance was predominant. The concentrations of HI and H_2SO_4 should be optimized for the most efficient operation. Figure 10 shows the thermal efficiency by changing H_2SO_4 concentrations. Data were from Figure 8 at 0.99 A dm^{-2} of current density. HI concentration in the catholyte was set at 16.7 mol $kg_{H2O}{}^{-1}$ and $I_2/HI = 1$. Thermal efficiency was decreased with increasing concentrations of H_2SO_4. In this case, it is not effective to concentrate H_2SO_4 solution using this technique. The heat demands required for the electrochemical cell were increased 61.7 kJ $mol_{H2}{}^{-1}$, from 10.3 to 17.2 mol $kg_{H2O}{}^{-1}$ of H_2SO_4, whereas the heat duty was decreased with only 8.6 kJ $mol_{H2}{}^{-1}$ by the difference. At this HI concentration, it is not effective to concentrate H_2SO_4 using this technique. Next, effects of HI concentration on the thermal efficiency were investigated at the lower H_2SO_4 concentrations (12.2–13.1 mol $kg_{H2O}{}^{-1}$), results of which are shown in Figure 11. There is an obvious maximum thermal efficiency, 42.1%, at around 14.3 mol $kg_{H2O}{}^{-1}$ of HI concentration in the catholyte. The basic hydrogen production system using an EED shows a thermal efficiency of 31.3% at 14.3 mol $kg_{H2O}{}^{-1}$ of HI concentration after the EED cell.

Conclusions

HI and H_2SO_4 were successfully concentrated using the electrochemical cell under low I_2 concentration. The final concentrations of HI and H_2SO_4 were 14.9 and 17.8 mol $kg_{H2O}{}^{-1}$

Table 2. Detailed Heat Demand Calculated by Heat/Mass Balance

Conditions	Current density	A dm^{-2}	0	0.20	0.40	0.99	2.96	5.93	11.9
	Total voltage	V	0.323	0.343	0.402	0.529	0.912	1.586	3.488
	Current	A				1.93×10^5			
Electricity	Recovery at H_2SO_4 concentration system	kJ $mol_{H2}{}^{-1}$				−9.0			
	Consumption at the electrochemical cell	kJ $mol_{H2}{}^{-1}$	57.2	61.0	72.4	96.9	170.8	300.9	667.9
	Required from outside of the system	kJ $mol_{H2}{}^{-1}$	48.2	52.0	63.4	87.9	161.8	291.9	658.9
Heat	H_2SO_4 decomposition	kJ $mol_{H2}{}^{-1}$				411.4			
	HI distillation	kJ $mol_{H2}{}^{-1}$				129.3			
	HI decomposition	kJ $mol_{H2}{}^{-1}$				13.8			
	Total heat demand without electricity	kJ $mol_{H2}{}^{-1}$				554.6			
	Heat demand for electricity	kJ $mol_{H2}{}^{-1}$	120.4	130.0	158.5	219.8	404.5	729.7	1647.3
	Total heat demand	kJ $mol_{H2}{}^{-1}$	675.0	684.6	713.1	774.3	959.1	1284.3	2201.8
	H_2 (High heat value)	kJ $mol_{H2}{}^{-1}$				285.8			
	Thermal efficiency	%	42.3	41.8	40.1	37.0	29.8	22.2	13.0

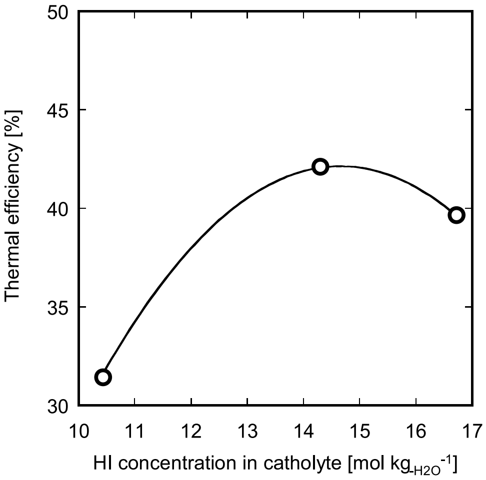


Figure 11. Effects of HI concentrations on total thermal efficiency.

at I_2/HI = 0.95. Both HI and H_2SO_4 were at higher concentrations than those reported for the liquid–liquid separation. The I_2 amount was about 25% of that in the former report. Intermediate products (HI, H_2SO_4) were concentrated at low concentration of recycling agent (I_2). These concentrations agree with the calculated values, indicating that electric energy was efficiently consumed. A higher H_2SO_4 concentration was preferred for the anolyte to suppress the side reaction of sulfur formation. The total voltage was sharply increased with increasing operation time. This was attributed to solution resistance caused by H_2SO_4 concentration in the anolyte. The cell structure should be improved to lower the solution resistance for efficient operation.

Effects of the application of the electrochemical cell were evaluated by the total IS process to obtain hydrogen in calculating the heat/mass balance. It is ineffective to concentrate H_2SO_4 using this technique at higher HI concentration (16.7 mol kg_{H2O}^{-1}) in the catholyte. However, thermal efficiency was calculated as 42.1% without electricity recovery from the waste heat by optimizing HI and H_2SO_4 concentrations. The current density of the electrochemical cell was 0.99 A dm^{-2} for the calculation.

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