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Dehydration through pervaporation from HIx solution (HI-H_2O-I_2 mixture) using a cation exchange membrane for thermochemical water-splitting iodine-sulfur process

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Abstract−Pervaporation (PV) of water from HIx solution (HI-H_2O-I_2 mixture) using Nafion-117 was evaluated aiming at the application to dehydrate the azeotropic composition in HI decomposition reaction of thermochemical IS process. PV experiment was carried out by using HI solutions of 40-65 wt% and an I_2/HI molar ratio of 0-3 in the feed at the room temperature. The permeation flux decreased with increasing HI weight fraction in the feed. The permeation flux is dependent on the I_2 concentration in the feed having an I_2/HI molar ratio. A long time PV experiment was carried out using I_2/HI molar ratio of 1 (in HI solution of 55.9%) in the feed at room temperature. It is expected that the permeation component in the permeate zone using the PV process was mainly H_2O, and H_2O permeation was constant with increasing operation time.

Key words: Pervaporation, Ion Exchange Membrane, Thermochemical Water-splitting, IS Process

INTRODUCTION

Hydrogen is an attractive fuel for the future because it is renewable as an energy resource and also flexible as an energy carrier. One of the promising methods for large-scale hydrogen production is thermochemical water-splitting using heat energy from nuclear, solar sources and so on. The IS (Iodine-Sulfur) process [Onuki et al., 1997] and the UT-3 (Ca-Fe-Br) process [Sakurai et al., 1992] have been investigated for thermochemical hydrogen production processes using heat energy from a nuclear source.

Since the IS process was first proposed by General Atomic Co. [Norman et al., 1981], it has been under investigation at JAERI (Japan Atomic Energy Research Institute), and hydrogen production with closed-cycle operation has been demonstrated in laboratory scale [Nakajima et al., 1998].

The cycle is composed of the following reactions:

$$I_2\ (l)+SO_2\ (g)+2H_2O\ (l)\rightarrow 2HI\ (aq.)+H_2SO_4\ (aq.) \tag{1}$$

$$H_2SO_4\ (g)\rightarrow H_2O\ (g)+SO_2\ (g)+(1/2)O_2\ (g) \tag{2}$$

$$2HI\ (g)\rightarrow H_2\ (g)+I_2\ (g) \tag{3}$$

The so-called Bunsen reaction (1) is an exothermic SO_2 gas absorbing reaction, which proceeds spontaneously in the temperature range of 20-100 °C. Sulfuric acid (H_2SO_4) decomposition reaction (2) is an endothermic reaction that proceeds in two stages: gaseous H_2SO_4 decomposes spontaneously into H_2O and SO_3 at 400-500 °C, and then SO_3 decomposes into SO_2 and O_2 at about 800 °C in the presence of a solid catalyst. Hydrogen iodide (HI) decomposition reaction (3) can be carried out in the gas phase or in the liquid phase. The process has such attractive characteristics that all chemicals circulate in the process as fluid, H_2SO_4 decomposition proceeds stoichiometrically with high conversion ratio and large entropy change, the temperature range of which is suitable for utilizing the nuclear heat supplied by VHTR (Very High Temperature Reactor System).

In HI decomposition reaction, hydrogen was produced by thermal decomposition of gaseous HI. HI is separated from HIx solution and then decomposed to produce hydrogen. The HIx solution (H_2O-HI-I_2 mixture) was produced in a Bunsen reactor. A simple option to realize the chemical change was the distillation of HIx solution and the gas phase thermal decomposition of HI. However, conventional distillation requires a considerable excess thermal burden because of the presence of an azeotropic composition in HI-H_2O system (the molal ratio of H_2O/HI is about 5). Also, the low equilibrium conversion of HI decomposition (ca 20% at 400 °C) imposed a large amount of HI circulation within the process, which results in the increase of thermal burden [Nakajima et al., 1998].

To raise the concentration efficiency of HIx solution and to improve the HI concentration process in thermochemical IS cycle, there are two kinds of applications on membrane technology [Onuki et al., 2001]. One is a concentration of HI using the membrane reactor to enhance the one-pass conversion of HI/I_2/H_2O equilibrium. The other is concerned with membrane application to enhance the HI molality of HI-I_2-H_2O mixture in order to facilitate the separation of pure HI. The second application is caused by the lack of capability to distill the HIx solution for a concentration of HI of more than 56%. To reach an HI concentration of 56% by conventional distillation to consume a great quantity of heat, the distillation process would be decreasing the overall thermal efficiency of the process.

One of the applications of membrane technology to concentrate HI molality is the process of electro-electrodialysis, which has been studying extensively [Onuki et al., 2001; Hwang et al., 2003; Kang et al., 2002, 2004]. Therefore, the other process of membrane application needs to be carried out as an alternative one. Pervaporation (PV) is one of the membrane techniques that is used to separate liquid mixture by partly vaporizing it through a membrane. The mixture

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is allowed to flow along one side of the membrane and a fraction of it is evolved in the vapor state from the opposite side, which is kept under vacuum condition by continuous pumping [Neel, 1991; Song et al., 2005]. The PV separation technique is recognized as an efficient separation method especially for liquid mixtures with an azeotrope or close boiling temperatures [Song et al., 2002]. From the view of energy consumption, the PV technique has already shown its capability to give a very significant energy savings as compared to more classic technologies (e.g. distillation, etc.) [Jonquieres, 2002].

In this study, Nafion-117 membrane was used to dehydrate the azeotropic composition of HI and HIx solution by PV process. And the possibility of the PV process to dehydrate the HI and HIx solution was evaluated.

EXPERIMENTAL

The hydriodic acid and iodine used in this experiment were supplied by Kanto Chemical Co. The feed of HI was prepared by dilute the hydriodic acid solution. The concentrations of HI solutions were set to 40-65%. Iodine dissolved in the HI solution, and the molar ratio of I_2/HI was adjusted with 0-3 considering the solubility of iodine at room temperature [Sakurai et al., 2000]. Then, it was a so-called HIx solution. Nafion-117 membrane purchased from DuPont Co. was used to the PV membrane without any treatment.

Fig. 1 shows a schematic diagram of the experiment apparatus.

The cooler in the cold trap used liquid nitrogen. The effective surface area of the membrane is 9.62×10^{-4} m^2 (a circular form with diameter of 3.5 cm). The amount of HI and HIx solution was 200 ml for the feed zone in the permeation cell. Table 1 shows the experimental conditions.

The PV experiment was carried out for 4-6 hours at room temperature and vacuum condition (pressure of 0.065 torr). The permeation rate was determined by measuring the weight change in the permeation zone. The composition of feed and permeated solution was analyzed by titration to calculate the HI and I_2 content in the feed and permeation zone.

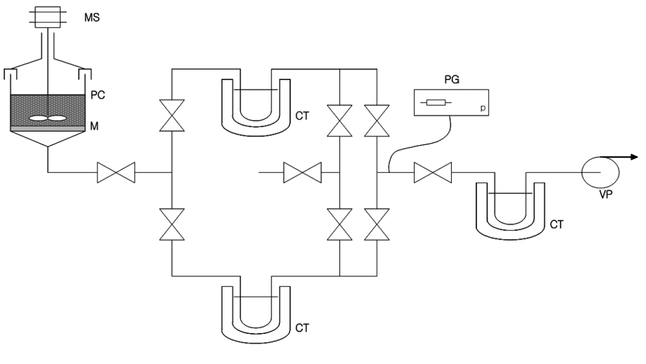

Fig. 1. Schematic diagram of experimental apparatus.

MS: Mixing stirrer	CT: Cold trap
PC: Permeation cell	PG: Pirani gauge
M: Membrane	VP: Vacuum pump

Table 1. The experimental conditions

Used membrane	Nafion-117
Effective membrane diameter	3.5×10^{-2} m
Membrane area	9.62×10^{-4} m^2
Operating temperature	25 °C
PV vacuum pressure	0.065 torr
HI feed concentration	20-65 wt%

The permeation flux was calculated by the following equation:

$$J=m/(A\cdot t) \tag{4}$$

where, J is permeation flux (g/m^2h), m is the weight change in the permeation zone (g), A is an effective surface area of membrane (m^2), and t is the experiment time (h).

The separation factor (α) was calculated by the following equation:

$$\alpha=(C_{H_2O}/C_{HI})_{permeate}/(C_{H_2O}/C_{HI})_{feed} \tag{5}$$

where, C_{H_2O} and C_{HI} were the weight fraction of H_2O and HI, respectively.

RESULTS AND DISCUSSION

1. Pervaporation

Fig. 2 shows the effects of HI weight fraction and I_2 concentration in the feed on the permeation flux. The permeation flux decreased with increasing HI weight fraction in the feed. The permeation flux with decreasing I_2 concentration at each HI weight fraction in the feed increased in the order 1>3>0.5>0 for the I_2/HI molar ratio in the feed. This means the permeation flux is dependent on the I_2 concentration in the feed having an I_2/HI molar ratio of 1, 0.5 and 0. However, the permeation flux examined at I_2/HI molar ratio of 3 in the feed decreased a little compared to that at I_2/HI molar ratio of 1. It seems that the non-solved I_2 block the permeation by its solidification in the HI solution at room temperature. Especially, in the case of I_2/HI molar ratio of 3, it was considered that iodine in HIx solution was extracted with solid by the variation of iodine sol-

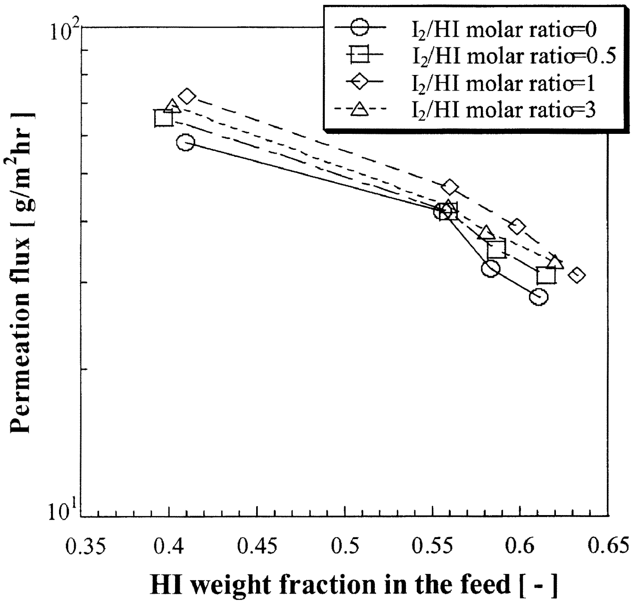

Fig. 2. Effects of HI weight fraction and I_2 concentration in the feed on the permeation flux.

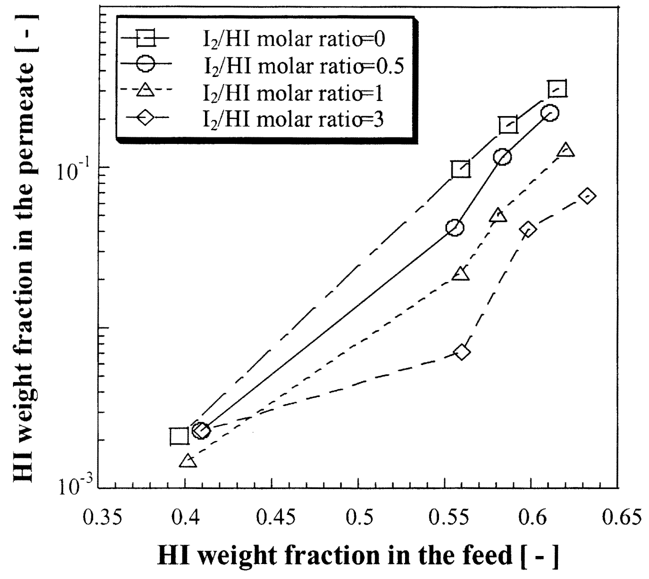

Fig. 3. Effects of HI weight fraction and I_2 concentration in the feed on the HI weight fraction in the permeation zone.

ubility in accordance with removing of a water-component.

Fig. 3 shows the effects of HI weight fraction and I_2 concentration in the feed on the HI weight fraction in the permeate zone. With increasing the I_2/HI molar ratio, the pervaporation equilibrium line was shifted forward right. It seems that the HI weight fraction in the permeate decreased with increasing I_2/HI molar ratio in the feed. The HI weight fraction in the permeate zone with increasing I_2 concentration at each HI weight fraction in the feed decreased in the order $3<1<0.5<0$ for the I_2/HI molar ratio in the feed. This means the HI weight fraction in the permeate zone is dependent on the I_2 concentration in the feed having a I_2/HI molar ratio of 1, 0.5 and 0.

From those results, it is expected that the permeation of HI increased with increasing HI weight fraction but decreased with increasing I_2 concentrate in the range of I_2/HI molar ratio of 0-1 in the feed.

Fig. 4 shows the effects of HI weight fraction in the feed on the separation factor. The separation factor (α) decreased with increasing HI weight fraction in the feed. The separation factor with increasing I_2 concentration at each HI weight fraction in the feed decreased in the order $1<3<0.5<0$ for the I_2/HI molar ratio in the feed by 60 wt%, and $3<1<0.5<0$ above 60 wt% HI feed concentration.

The separation factor (α) had about 3.1×10^2, 28-180, 10-50 and 5-35 for the HI weight fraction of 0.4, 0.55, 0.58 and 0.61 (with I_2/HI molar ratio of 0-3) in the feed, respectively.

2. Long Time Pervaporation Experiment

A long term PV experiment was carried out to evaluate the lifetime of Nafion-117 in the HIx solution at the room temperature.

Fig. 5 shows the relationship between permeation concentration of each component and operation time in the PV process using I_2/HI molar ratio of 1 (in HI solution of 55.9%) in the feed.

The permeation concentration of H_2O has almost the same value with increasing operation time. The permeation concentration of I_2 was large at the initial time, and decreased until 20 min, and then had almost the same value with increasing operation time. The permeation concentration of HI increased until 60 min, and then had the almost same value with increasing operation time.

From this result, it is expected that the permeation component in the permeate zone using PV process was mainly H_2O, and H_2O permeation was constant with increasing operation time.

Fig. 6 shows the relationship between permeation flux, separation factor and operation time in the PV process by using an I_2/HI molar ratio of 1 (in HI solution of 55.9%) in the feed.

The permeation flux increased until 40 minutes, and decreased until 80 minutes, and hereafter had the almost same value with progressing the operation time. The separation factor was comparatively large at the initial time, but decreased until 80 minutes, and hereaf-

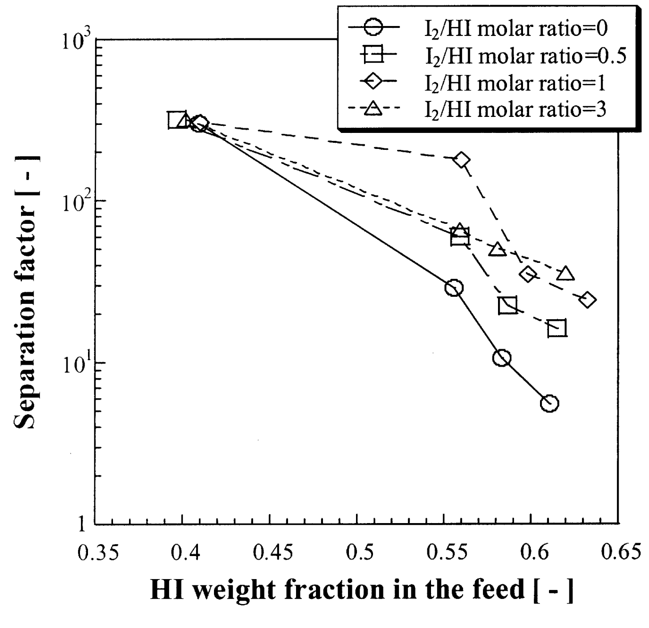

Fig. 4. Effects of HI weight fraction in the feed on the separation factor.

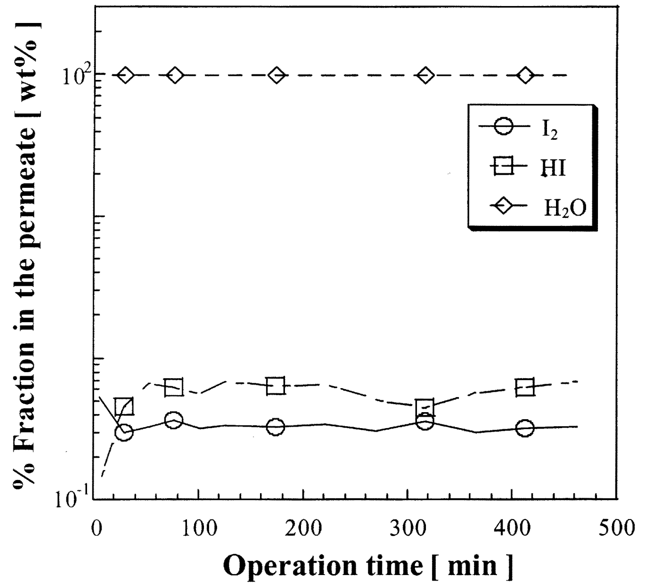

Fig. 5. Relationship between permeation concentration of each component and operation time in the PV process using I_2/HI molar ratio of 1 (in HI solution of 55.9%) in the feed.

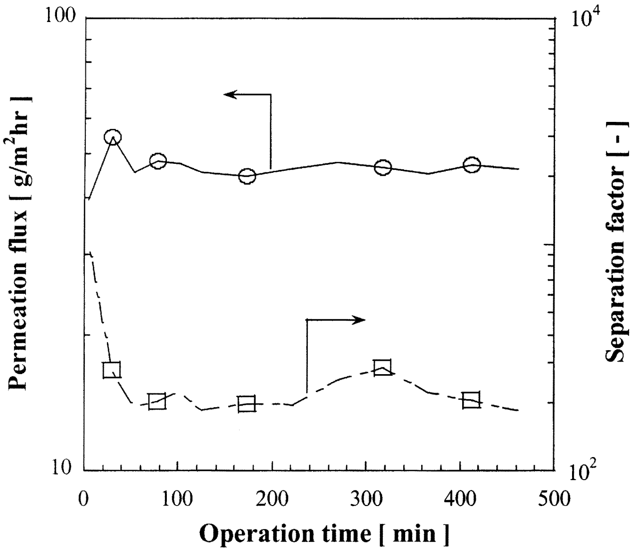

Fig. 6. Relationship between permeation flux, separation factor and operation time in the PV process using I_2/HI molar ratio of 1 (in HI solution of 55.9%) in the feed.

ter had the almost same value with increasing operation time. The separation factor (α) had a range of 200-300 within the operation time. It is supposed from this result that the Nafion-117 would be suitable in the PV process using HIx solution with its stability.

From above results, it is obtained that PV process using Nafion-117 would be useful with proposing the possibility to dehydrate the azeotropic composition of HI and HIx solution.

CONCLUSIONS

1. Pervaporation of water from HIx (H_2-H_2O-HI) solution using Nafion-117 was examined to dehydrate the azeotropic composition in HI decomposition reaction of thermochemical IS process.

2. PV experiment was carried out using HI solutions of 40-65% and the I_2/HI molar ratio of 0-3 in the feed at the room temperature. The permeation flux decreased with increasing HI weight fraction in the feed. The permeation flux is dependent on the I_2 concentration in the feed having the I_2/HI molar ratio.

3. A long term PV experiment was carried out using I_2/HI molar ratio of 1 (in HI solution of 55.9%) in the feed at the room temperature. The permeation component in the permeate zone using PV process was mainly H_2O. The separation factor (α) had a range of 200-300 within the operation time.

4. It is supposed from the results that the Nafion-117 would be suitable in the PV process using HIx solution with its stability. And PV process using Nafion-117 would be useful with proposing the possibility to dehydrate the azeotropic composition of HI and HIx solution.

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