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Optimization of the process parameters of an electrochemical cell in the IS process

Mikihiro Nomura[a,*], Hiroyuki Okuda[b], Seiji Kasahara[b], Shin-ichi Nakao[a]

[a] *Department of Chemical System Engineering, Faculty of Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*
[b] *Department of Advanced Nuclear Heat Technology, Oarai Research Establishment Japan Atomic Energy Research Institute, Niibori 3607, Narita-cho, Oarai-machi, Higashiibaraki-gun, Ibaraki 311-1394, Japan*

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Abstract

One of the key reactions for efficient hydrogen production using the water-splitting iodine–sulfur (IS or S–I) process is the Bunsen reaction ($SO_2 + I_2 + 2H_2O = H_2SO_4 + 2HI$). The Bunsen reaction was examined using an electrochemical cell with a cation exchange membrane as the separator. The optimal molalities of anolyte and catholyte were evaluated by total thermal efficiency using the heat/mass balance of the IS process. The I_2/HI ratio had little effect on the required total voltage; the I_2/HI ratio can be reduced to 0.5 without decreasing the total thermal efficiency. On the other hand, HI and H_2SO_4 molality greatly affected the total thermal efficiency. The total thermal efficiency increased with increasing HI molality up to $16.7\,\mathrm{mol\,kg^{-1}_{-H_2O}}$ and the maximum thermal efficiency was found at $15.3\,\mathrm{mol\,kg^{-1}_{-H_2O}}$ of H_2SO_4. Membrane resistances are very important parameters affecting the efficiency. The total thermal efficiency increased by 3.0% at a current density of the electrochemical cell of $10.0\,\mathrm{A\,dm^{-2}}$ by increasing the operating temperature from 313 to 363 K.

Keywords: Electrochemistry; Energy; Membranes; System engineering; Hydrogen production IS (S–I) process; Thermal efficiency

1. Introduction

Hydrogen is an attractive energy carrier for future transportation systems and is easily converted to electricity using a fuel cell. There are various processes proposed for an effective hydrogen production from water, such as electrolysis or photochemical production. Thermochemical water splitting using solar or nuclear heat is a promising method for large-scale hydrogen production without carbon dioxide emission. Many processes for thermochemical hydrogen production have been proposed since the 1960s (Funk, 2001). A group of Japan Atomic Energy Research Institute (JAERI) has been developing the Iodine–Sulfur (IS or S–I) process as one of thermochemical hydrogen production methods for use with the high-temperature gas-cooled reactor (Onuki et al., 1990). JAERI conducted continuous hydrogen production using the IS process using a glass-made apparatus (Nakajima et al., 1998; Kubo et al., 2004). Production of $31.5\,\mathrm{L\,H_2\,h^{-1}}$ of hydrogen was successfully obtained for 21 h to develop operating procedures for the IS process. The IS process consists of the three reactions described below.

$$SO_2 + 9I_2 + 16H_2O = (H_2SO_4 + 4H_2O) + (2HI + 8I_2 + 10H_2O) \quad (1)$$

$$H_2SO_4 + 4H_2O = SO_2 + 5H_2O + 0.5O_2 \quad (2)$$

$$2HI + 8I_2 + 10H_2O = H_2 + 9I_2 + 10H_2O \quad (3)$$

The first reaction is called the Bunsen reaction. Water reacts with SO_2 and I_2 to form a H_2SO_4 and HI solution. General atomics (GA) (Norman et al., 1981, 1982) proposed and demonstrated that these acids could be separated by density

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* Corresponding author. Tel./fax: +81 3 5841 7346.
E-mail address: lscathy@chemsys.t.u-tokyo.ac.jp (M. Nomura).

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if sufficient excess iodine is added to form two liquid phases. An excess of I_2 and water is required for the reaction mixtures as shown in reaction (1). H_2 and O_2 are obtained by heat decomposition of these acids as indicated by reactions (2) and (3), respectively. Decomposed I_2 and SO_2 are recycled to the Bunsen reaction. I_2 and SO_2 act as catalysts for the decomposition reaction of water and the highest temperature required decreased to approximately 1000 K (reaction (2)) for the IS process.

This process must be operated efficiently for efficient hydrogen production. There have been several methods reported to simplify the IS process. The group of GA (Norman et al., 1981) demonstrated an extractive distillation method using phosphoric acid to reduce vaporized water before reaction (3). A group at Aachen University (Roth and Knoche, 1989) proposed a reaction distillation where the decomposition reaction of HI was employed to simplify the process. The total thermal efficiency calculation is important to estimate the effect of the improvements. Norman et al. (1982) claimed a thermal efficiency of 47% by calculating heat/mass balance of the process featuring an extractive distillation method for the HI distillation procedure. Kasahara et al. (2003) reported a thermal efficiency of 57% under ideal conditions using two membrane separation techniques (an electro-electrodialysis (EED) and a hydrogen permselective membrane reactor (HPMR)). The first is an EED to concentrate the HI solution using a cation exchange membrane (e.g., Onuki et al., 2000; Hwang et al., 2003). Hwang et al. (2003) successfully concentrated the HI solution to over 21 wt% ($15\,\mathrm{mol\,kg^{-1}_{-H_2O}}$) of HI at a temperature of 393 K. The second membrane technique is the application of a HPMR for the decomposition reaction of HI. The silica membrane deposited at $T = 873$ K was stable for 24 h with a H_2–HI–H_2O atmosphere at a temperature of 723 K (Hwang et al., 2000). The effect of hydrogen extraction on reaction (3) was demonstrated by Nomura et al. (2004c) using silica membranes.

It is important to reduce the I_2 and water at the liquid–liquid separator after the Bunsen reaction because excess I_2 and water are added by this procedure. When the liquid–liquid separator after the Bunsen reaction is employed, it is necessary to recycle 8 mol of I_2 to obtain 1 mol of hydrogen as shown in the reaction equation (1). Recently, an electrochemical cell (EC) featuring a cation exchange membrane has been applied to the Bunsen reaction to reduce the recycling of I_2. An EC is a combination of an acids separator and concentrator of HI and H_2SO_4. Fig. 1 shows a schematic diagram of the EC apparatus. HI and I_2 solution is introduced as a catholyte, and SO_2 solution is supplied as an anolyte. The reactions at both sides of the electrodes are as follows:

At the anode side electrode:

$$SO_2 + 2H_2O = H_2SO_4 + 2H^+ + 2e^- \tag{4}$$

At the cathode side electrode:

$$I_2 + 2H^+ + 2e^- = 2HI \tag{5}$$

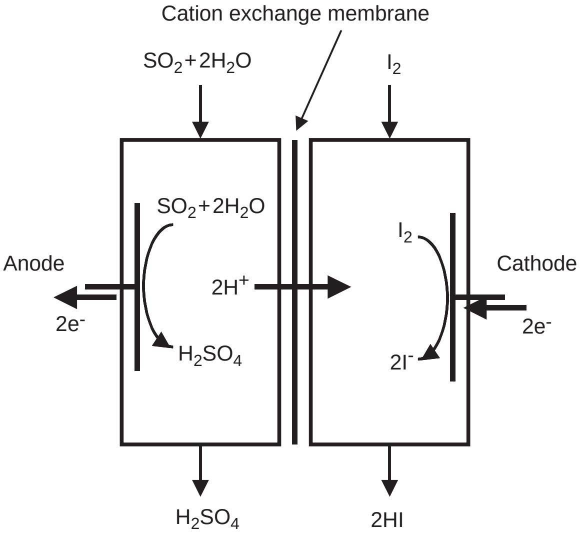

Fig. 1. A schematic diagram for the electrochemical cell (EC) for the Bunsen reaction.

Total (the Bunsen reaction):

$$SO_2 + I_2 + 2H_2O = H_2SO_4 + 2HI \tag{6}$$

The H_2SO_4 and HI solutions are obtained separately on either side of the cation exchange membrane. Therefore, the I_2 and H_2O required for a liquid–liquid separator can be reduced. We reported that the Bunsen reaction was successfully employed using the EC reduced I_2 recycling by 93% (Nomura et al., 2004a). The excess of H_2O was also reduced by 69% (Nomura et al., 2004b). The total initial cost can be reduced by 20% by applying the EC due to the combination of the Bunsen reactor and the liquid–liquid separator (Nomura et al., 2003). However, EC evaluations only considered the HI concentration and decomposition procedure (Nomura et al., 2004b). Therefore, the optimum operating conditions for this EC were not clear. In this report, the effects of an EC on the IS process were evaluated using the heat/mass balance calculations for both HI and H_2SO_4 procedures, and operating conditions were optimized for total thermal efficiency to obtain hydrogen.

2. Experiment results

The detailed experimental procedures have been described previously (Nomura et al., 2004a). The experiment was performed at a temperature of 313–363 K with constant current, controlled by Potentiostat/Galbanostat HA-305 (the Hokuto Denko, Japan). The cation exchange membrane was Nafion 117 (Dupont, USA, effective membrane area $5.06 \times 10^{-4}\,\mathrm{m^2}$). Graphite felts provided by Toyobo (Japan) were used as electrodes on both sides of the EC. The HI and the H_2SO_4 solutions were diluted to the specified concentration using deionized water, and poured into 200 ml flasks. The solutions were circulated between the membrane reactor cells and flasks by a roller pump (RP-100, Tokyo Rikakiki Co.