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Evaluation of the membrane properties with changing iodine molar ratio in HIx (HI–I_2–H_2O mixture) solution to concentrate HI by electro-electrodialysis

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Abstract

The electro-electrodialysis (EED) experiment was carried out to concentrate HI from HIx (HI–H_2O–I_2 mixture) solution, which may be achieved by thermochemical water splitting IS (iodine–sulfur) process. The molar ratios of the HIx solution were HI:H_2O:I_2 = 1:6.0:0.5 (I_2-0.5 solution), 1:5.8:1 (I_2-1 solution) and 1:6.4:2 (I_2-2 solution). EED cell are composed of the collector, electrode and electrolyte. The carbon plate, Nafion 117, which was cation exchange membrane and the activated carbon cloth used as an collector, electrolyte and electrode, respectively. In the catholyte, the HI mole fractions increased and I_2 mole fractions decreased by EED operation. The cell voltage reached to 0.24 V, 0.29 V and 0.40 V for I_2-0.5 solution, I_2-1 solution and I_2-2 solution after 10 h EED operation, respectively. The electro-osmosis coefficient decreased from 1.49 mol/Faraday to 0.93 mol/Faraday and proton transport number increased from 0.74 to 0.84 with an increase of iodine molar ratio. It has been observed that the rate of enhancement in HI concentration is also affected by membrane properties.

Keywords: Hydrogen production; IS process; HI concentration; Electro-electrodialysis; Cation exchange membrane

1. Introduction

Hydrogen is an attractive fuel for the future because it is renewable as an energy resource and it is also flexible as an energy carrier. One of remarkable methods for large-scale hydrogen production is thermochemical water decomposition using heat energy from nuclear, solar and other sources.

IS (iodine–sulfur) process [1–4] have been investigating for the thermochemical hydrogen production processes using heat energy from nuclear. In the KIER (Korea Institute of Energy Research), IS process is under investigation with KAERI (Korea Atomic Energy Research Institute) [5]. The cycle is composed of the following reactions:

$$I_2\,(l) + SO_2\,(g) + 2H_2O\,(l) \rightarrow 2HI\,(aq.) + H_2SO_4\,(aq.) \quad (1)$$

$$H_2SO_4\,(aq.) \rightarrow H_2O\,(g) + SO_2\,(g) + (1/2)O_2\,(g) \quad (2)$$

$$2HI\,(g) \rightarrow H_2\,(g) + I_2\,(g) \quad (3)$$

The so-called Bunsen reaction (1) is an exothermic SO_2 gas absorbing reaction, which proceeds spontaneously in the temperature range of 20–120 °C. Sulfuric acid (H_2SO_4) decomposition reaction (2) is an endothermic reaction, which proceeds in two stages, i.e. 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 850 °C in the presence of a solid catalyst [2]. Hydrogen iodide (HI) decomposition reaction (3) can be carried out in the gas phase or in the liquid phase.

In the IS process, HI is separated form HIx solution (HI–H_2O–I_2 mixture) that was supplied from Bunsen reaction and then decomposed to produce hydrogen. Simple option to realize the chemical change is the distillation of HIx solution and the gas phase thermal decomposition of HI. However, because of the presence of azeotropic composition in HI–H_2O mixtures

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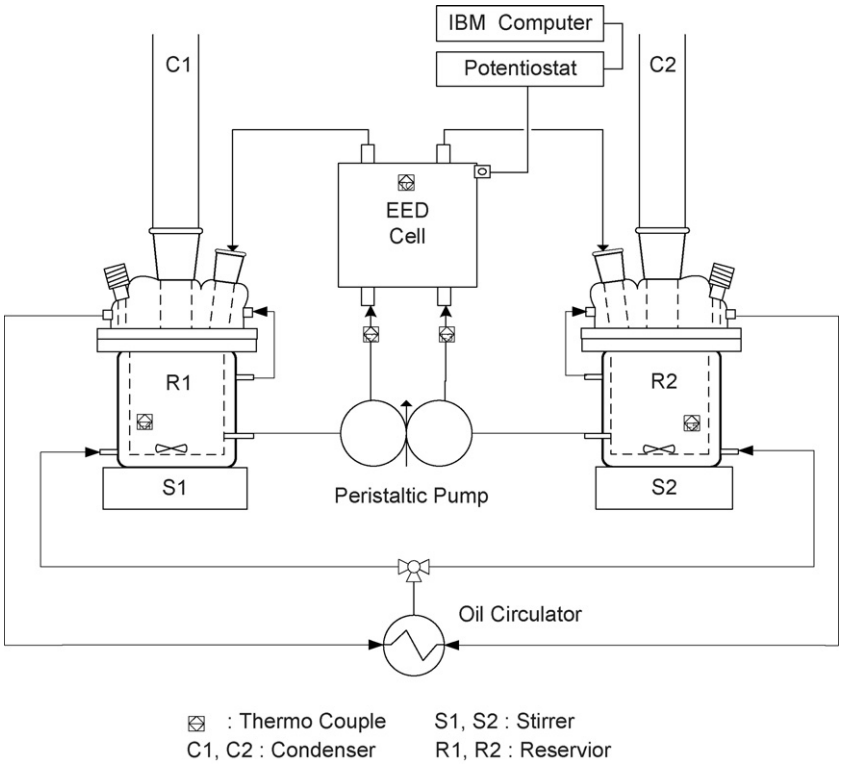

Fig. 1. Experimental apparatus for EED.

(the molar ratio of HI:H_2O = 1:5), the distillation requires a lot of excess thermal burden [6,7]. In order to overcome this problem, in JAEA (Japan Atomic Energy Agency), the EED process employed to concentrate HI from HIx solution and reported the efficiency of IS process base on EED as above 50% [8,9]. However, there are many parameters in EED experiment that have effect on the efficiency of the IS process. The parameters are composition of HIx solution, experimental temperature and properties of the material such as electrolyte (ion exchange membrane) and electrode and so on.

In our previous research, it was reported that the effect of temperature with iodine molar ratio to concentrate HI from HIx solution [10–12]. The purpose of this study is to evaluate the effect of membrane properties (Nafion 117) as well as the change in the molar ratio of I_2 (0.5–2) in HIx solution on the rate of enhancement in HI concentration.

2. Experimental

2.1. Preparation for HIx solution

The hydroiodic acid (Yakuri Co., 57%) and iodine (Junsei Co., 99%) were used as the HIx solution source to meet the certain molar ratios. The iodine dissolved into hydroiodic acid with increasing temperature to make molar ratio of HIx (HI:H_2O:I_2 = 1:6.0:0.5–2). Potassium iodide (Junsei Co., 99.5%), sodium hydroxide (Shinyo Co., 96%) and sodium thiosulfate pentahydrate (Junsei Co., 99%) were used for the titration.

2.2. Experimental setup for electro-electrodialysis (EED)

Fig. 1 shows the EED experimental apparatus. The EED experimental setup consisted of following main parts. Reservoirs with glass tubes were formed by double jacket to control the temperature in anolyte and catholyte. Peristaltic pump used to control the flow rate of HIx solution. Vapor pressure of HIx solution is known to increase steeply with increasing HI molality in the range higher than ca. 10 mol/kg. So, in order to avoid the pressure increase in the glass reservoirs and also to minimize the dissipation of HI vapor, the condensers were equipped on the top of both reservoirs. Thermocouples were fitted in the cell, reservoirs and glass tube lines which located in the cell inlet to control the experimental temperature.

An activated carbon cloth was used as electrode. The BET surface area was 700 m^2/g and average pore diameter was 24 Å. The commercial cation exchange membrane (Nafion 117) was employed in a cell. Fig. 2 illustrates the EED cell. In this study, the Teflon was used as gasket. In the EED, the electrode reaction was the redox reaction of iodine–iodide ions as follows:

$$I_2 + 2e \underset{\text{Anode}}{\overset{\text{Cathode}}{\rightleftarrows}} 2I^-$$

Therefore, with the help of selective proton permeation through the membrane, it is expected that the aimed “concentration” is possible in the sense that HI mole fraction of catholyte increase while that of anolyte decrease.