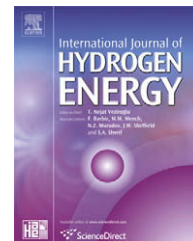


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Concentration of HIx solution by electro-electrodialysis using Nafion 117 for thermochemical water-splitting IS process

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ARTICLE INFO

Article history:

Received 19 February 2008

Received in revised form

2 September 2008

Accepted 18 September 2008

Available online 5 November 2008

Keywords:

Electro-electrodialysis

HIx solution

Nafion

IS process

Thermochemical hydrogen production

ABSTRACT

An experimental study of applying electro-electrodialysis (EED) for improved HI concentration in the HIx solution, a mixture of HI–I₂–H₂O of approximately quasi-azeotropic compositions has been carried out in the conditions of around 90 °C and using Nafion 117 and graphite electrodes. A range of 25–80% increase in initial current efficiency of HI molality in catholyte is measured with the use of EED. In general, the efficiency increases with increasing iodine molality and weight ratio of anolyte solution to catholyte solution. The EED performance degrades in time. In some cases, the HI concentration limits are observed. Electric conductivity of the HIx solution, overvoltage of electrode reaction, and the membrane voltage drop is measured in a temperature range of 20–120 °C. It is found that the EED cell voltage, which is an important cell performance parameter, is governed by the membrane voltage drop.

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1. Introduction

Thermochemical hydrogen production processes have been studied since 1970s for large-scale hydrogen production using heat with temperature of as high as 1000 °C, which can be supplied by nuclear energy from High Temperature Gas-cooled Reactor or solar energy. Of many processes studied, the iodine–sulfur process proposed by General Atomics [1] has attracted much interest and intensive studies.

One of the technical challenges of making hydrogen production efficient with the sulfur–iodine process remains to be the successful development of an efficient scheme of separating hydrogen iodide (HI) from HIx solution, a mixture of HI–I₂–H₂O. The HIx solution, which is produced in the Bunsen process reactor, is nearly quasi-azeotropic. Application of the

conventional fractional distillation to separating HI from the solution is energy intensive due to the necessity of evaporating the solvent water. Alternative distillation methods including the extractive distillation using phosphoric acid [2] and the reactive distillation in pressurized condition [3–5] have been investigated. In addition, application of membrane technologies has also been considered such as the pervaporation [6–8] and the electro-membrane process called electro-electrodialysis (EED) [9–12].

The concept of the EED, on which this paper is focused, separates HI from the HIx solution while avoiding evaporation of water. It increases the HI molality in the solution to over the level of quasi-azeotropic composition by combining the redox reaction of iodine–iodide ion at electrodes and the selective permeation of proton through a separation diaphragm (Fig. 1).

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Nomenclature

t_+	transport number of proton, dimensionless
β	ratio of permeated quantities of water to proton, dimensionless
F	Faraday constant, C/mol
ΔM_j^c	molar change of j -component in catholyte, mol
I	electric current, A
R	resistance of membrane, Ω
t	time, s
Δm	molality increase, dimensionless
$m_{\text{HI},0}^c$	initial HI molality in catholyte, mol/kg
m_{HI}^c	HI molality in catholyte, mol/kg
Q_e	normalized quantity of electricity, dimensionless
$M_{\text{HI},0}^c$	feed HI in catholyte, mol
η_Q	current efficiency, dimensionless
ϕ	overvoltage of anode or cathode, V

The HI molality of quasi-azeotropic HIx solution is about 10 mol/kg, which varies with iodine molality and pressure [13–15]. In spite of the already very high electrolyte concentration, the feasibility of its further improvement was demonstrated in beaker-scale experiments using a commercial styrene-divinyl benzene type cation exchange membrane as the separation diaphragm and glassy-carbon as the electrode material [9]. Recently, Hong et al. [10–12], using Nafion 117 as the separation diaphragm, reported the effects of operation temperature and iodine molality on the membrane permselectivity in the EED conditions.

Because of its exceptional thermal and chemical stability, the perfluorinated cation exchange membrane of the commercially available cation exchange membranes is expected to be more applicable than other synthetic polymer membranes to operate in harsh process conditions such as the present EED condition. In the present study, further experiments are carried out using Nafion to examine its permselectivity under various EED conditions, which might well be indicated by the current efficiency of the HI molality increase in catholyte. Another important performance indicator of the EED is the cell voltage. In the present study, in order to gain technical insight required to optimize cell design and improve component performance detailed breakdown of the overall

cell voltage has been examined by measuring the contributing factors in an EED cell made of Nafion and graphite electrodes.

2. Experiments

2.1. Test solutions and membrane

The 55–58 wt% hydriodic acid supplied by Kanto Chemical Co., INC., the 67 wt% hydriodic acid by Merck Ltd., and the 99.8wt% iodine by Kanto Chemical Co., INC. were used as received to prepare HIx solutions to approximately quasi-azeotropic compositions with I_2/HI molar ratios ranging from 1 to 4. The quasi-azeotropic compositions of HIx solution were estimated based on Engels et al. [16]. Nafion 117 was provided by E.I. du Pont de Nemours & Company as the separation diaphragm.

2.2. Concentration by electro-electrodialysis

2.2.1. Experimental setup

The experimental setup for the EED experiments consists of an EED cell, reservoirs for anolyte and catholyte solutions, two pumps, and a DC power supply as shown in Fig. 1. A filter-press type cell shown in Fig. 2 was used as the EED cell which consists of two electrodes made of isotropic graphite provided by TOYO TANSO Co., Ltd., two rubber gaskets by Viton® and a separation diaphragm. The effective area of the membrane is 80 cm² and the gasket thickness is 2.0 mm. A Teflon mesh is inserted in each compartment as a spacer between membrane and electrode to support the membrane and also to avoid stagnation. Rubber heaters are used to control the operation temperature of the EED cell. Glass reservoirs for anolyte solution and catholyte solution are connected with each compartment of the cell with Teflon tubes. Peristaltic pumps are used for circulation of the solutions. The glass reservoirs are coated with tin oxide type transparent heaters and placed on hot-plate type magnetic stirrers. Programmable DC Power source supplied by TAKASAGO LTD. feeds direct current to the cell in addition to monitoring the cell voltage.

2.2.2. Concentration experiments

The concentration experiments were carried out under atmospheric pressure and at constant current density.

Anolyte and catholyte solutions fed to the reservoirs were, at first, heated while circulating between the cell and the reservoirs for about 1 h. After the system reached steady state of prescribed temperature, direct current was supplied with galvanostatic mode. In the EED operation, the cell voltage was continuously recorded and the sampling of the solutions was carried out periodically to monitor the concentration change. The current supply was terminated when irregular phenomena occurred such as solid iodine precipitation in the anolyte solution or boiling of the catholyte.

In all the concentration experiments, identical HIx solutions were used as the feeds for anolyte and catholyte. The test temperature was 90–100 °C. The applied current density ranged from 100 to 200 mA/cm². Composition of the test solution was analyzed using an automatic potentiometric titrator (COM-2500, Hiranuma Sangyo Co., Ltd., Japan). NaOH solution (0.1 mol/d m⁻³) and Na₂S₂O₃ solution (0.1 mol/d m⁻³)

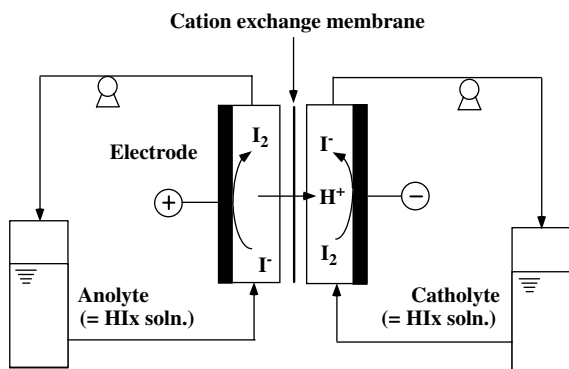


Fig. 1 – Electro-electrodialysis of HIx solution.

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