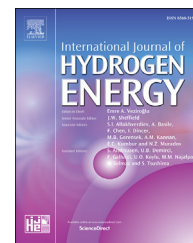


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# Decomposition of hydriodic acid by electrolysis in the thermochemical water sulfur–iodine splitting cycle

Shaojie Xu, Yong He<sup>\*</sup>, Biyi Huang, Yanwei Zhang, Zhihua Wang, Kefa Cen

State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, PR China

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## ABSTRACT

Although several technologies, such as reactive distillation and catalytic membrane reactor, have been proposed to improve HI conversion efficiency, they still experience several challenges for the application in HI section. In this study, an electrochemical cell was employed for hydriodic acid decomposition under the presence of iodine. Several commercial proton-exchange membranes (PEMs), namely, Nafion 117 and Nafion 115, were used as separators for the electrochemical cell. Anodization of iodide anion occurred at the graphite electrode in the anode compartment. Hydrogen was generated by the reduction reaction of hydrogen cations, which migrated from anolyte to catholyte. In electrolysis experiments, PEM showed good performance in terms of high transport number of proton and low iodine permeation. Several parameters, such as operating temperature, HI molarity, and  $I_2$  molarity in anolyte, which affected current efficiency, iodine permeance, and electric resistance of test cell, were investigated. High operating temperature and  $I_2$  molarity in anolyte enhanced the permeability of iodine, which had several negative influences on electrochemical cell performance. Although current efficiency was negatively affected by increasing temperature and  $I_2$  molarity, it still remained above 0.85 in the range of 30 °C–75 °C. Ohmic resistance, which is a component of cell resistance, offered by PEM was investigated with Nafion 117 and 115. Apart from graphite plates, activated carbon papers were adopted as electrodes to reduce the overpotentials due to their high specific surface characteristic.

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## Introduction

The utilization quantity of fossil energy has sharply increased in the past several decades and has caused considerable serious issues, including limited resources, environmental pollution, and global warming. All of these issues can prevent industrial development and threaten the survival of human

society. Hydrogen, which is considered a substitute for increasingly exhausted fossil fuels, is a clean and zero-carbon emission energy carrier. Scalable, efficient, and low-cost technologies for hydrogen production are the pillars of hydrogen economy development. Although petrochemical processing is the primary method used for hydrogen generation at present, it is not sustainable due to limited natural resources. Thus, several other methods, such as electrolysis,

<sup>\*</sup> Corresponding author.

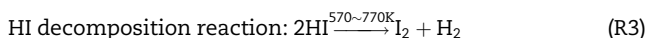
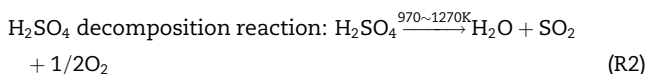
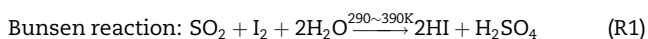
E-mail address: [heyong@zju.edu.cn](mailto:heyong@zju.edu.cn) (Y. He).

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photolysis, and thermochemical cycles, using water as raw material, have huge development advantages and latent capacities.

The concept of thermochemical water splitting cycles was first proposed by Funk and Reinstrom [1] in 1964, in which the heat required is matched with solar heat [2] or nuclear energy [3]. The thermochemical methods currently include sulfur–iodine [4], copper–chlorine [5], UT-3 [6], and hybrid–sulfur cycles [7]. After a variety of assessments by General Atomics Co., the sulfur–iodine thermochemical cycle (SI or IS) was identified as the most promising hydrogen production process [8]. The SI process contains three essential reactions as shown below:

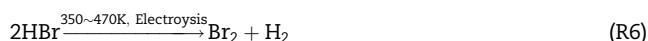
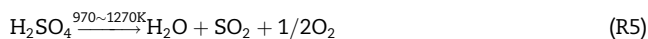
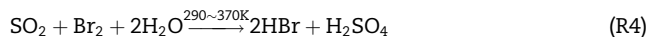


In the Bunsen reaction,  $\text{SO}_2$  gas reacts with aqueous  $\text{I}_2$  to form the mixture acid solution of sulfuric and hydriodic acids [9,10]. The mixture solution can be separated into two immiscible phases in present of excess amounts of iodine, namely, the light phase ( $\text{H}_2\text{SO}_4\text{--H}_2\text{O}$ ) and heavy phase ( $\text{HI--I}_2\text{--H}_2\text{O}$ ) with different densities. After purification, concentration, and separation, sulfuric and hydriodic acids are fed to  $\text{H}_2\text{SO}_4$  and HI decomposition reactors, respectively.  $\text{H}_2$  and  $\text{O}_2$  are collected as products, and  $\text{SO}_2$  and  $\text{I}_2$  are returned to the Bunsen reactor as recycling agents. The inputs of the entire SI cycle hydrogen production system are only water and heat [11].

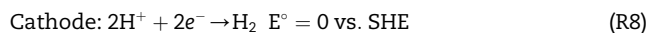
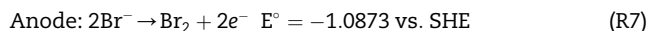
The HI decomposition section is the complex part in the SI cycle system. Because of the pseudo-azeotropy of  $\text{HI--I}_2\text{--H}_2\text{O}$  solution [12] and low-equilibrium conversion ratio of HI (ca. 20%, 450 °C [13]), considerable energy is consumed for HI concentration, separation, and decomposition steps. Two main technological routes are used to improve the thermal efficiency of the HI decomposition section. The first route employs an electro-electrodialysis (EED) cell to enrich the HI concentration up to hyper-azeotropy [14]. In this method, the hyper-azeotropic solution is fed to a normal rectification column to obtain high HI mole fraction in the distillate. Through Environmental Simulation Program software simulation, Guo and Kasahara [15] reported that 1.0 MPa is the optimum pressure of a normal HI distillation column by considering the thermal efficiency of the SI process. Kang [16] used an EED stack consisting of 10 cells with 830  $\text{cm}^2$  active area per cell to achieve an effective level of HI concentration with a hydrogen production rate of 10  $\text{L h}^{-1}$ . For EED stacks coupled with a normal distillation model, too many required EED stacks and the pressurized conditions in the HI distillation column are the challenges of large-scale hydrogen generation. Another method involves feeding unpre-concentration  $\text{HI}_x$  solution to a reactive distillation column, in which hydrogen separation and HI decomposition occur simultaneously [17]. Although several thermodynamic models for  $\text{HI}_x$  solution have been proposed and some reactive distillation processes have

been designed and simulated [18], no details about the experimental device and research results are presented. The reactive distillation column, force pumps, and pipes operating at high temperature (200 °C–300 °C) and pressure (50 bar) should have excellent corrosion resistance on  $\text{HI}_x$  solution, which appears to be the vital problem in the SI process.

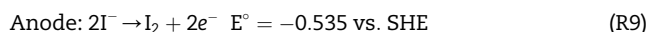
Schütz and Fiebelmann invented the Ispra Mark-13 sulfur–bromine cycle [19], which consists of the three following reactions:



For the electrochemical step, the reactions at the anode and cathode are expressed as follows:



Velzen and Langenkamp built a bench-scale continuous model plant in 1978 with a hydrogen production rate of 100  $\text{L h}^{-1}$  and 37% process efficiency [20]. A rectangular cell is used in the plant, and the cell voltages are 0.85 V at 200  $\text{mA cm}^{-2}$  and 1.03 V at 500  $\text{mA cm}^{-2}$  at 77 °C with 45 wt% HBr [21]. If bromine is replaced with iodine, and hydroiodic acid is decomposed by electrolysis, the anode reaction is expressed as follows:



Thus, the overall reaction in the electrolyzer is



The theoretical voltage for HI electrolysis is 0.53 V based on the reversible voltages for anode iodide ion oxidation and cathode proton reduction. Compared with the voltage for conventional water electrolysis (1.23 V) [22] and HBr electrolysis (1.087 V), the lower voltage for HI electrolysis provides more prospects in electrical power cost reduction. Maskalik and Pittsburgh invented a hydriodic acid-anode-depolarized hydrogen generator and reported that the anode potential is obtainable at  $-0.3$  V at 950  $\text{mA cm}^{-2}$  at 25 °C with 0.9 mol HI and 50 wt%  $\text{H}_2\text{SO}_4$  [20]. For the EED/thermal decomposition technology, the voltage of EED cell is about 0.4 V with a current density of 100  $\text{mA cm}^{-2}$  at 60 °C [23], which is lower than that for HI electrolysis (1.2 V) under the same conditions. However, HI electrolysis can replace the existing EED/thermal decomposition technologies considering the low HI thermal decomposition rate (ca. 22%, 500 °C) and the extra required energy for HI distillation. The process efficiency can be improved if halogen is changed to iodine.

Therefore, electrolysis could be used as an alternative for HI decomposition in SI cycle. Fig. 1 shows the principle of HI decomposition by a cell with the aid of a D.C. power source. Iodide ions are electrochemically oxidized to form iodine at the anode. Protons under the function of electric field migrate

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