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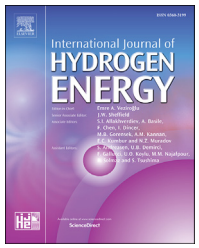

Numerical analysis of the electrochemical Bunsen reaction for hydrogen production from sulfur–iodine cycle

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ABSTRACT

The sulfur–iodine (S-I) water-splitting cycle is one of the most promising hydrogen production methods. The Bunsen reaction in the cycle affects the flowsheet complexity and thermal efficiency, but an electrochemical technique has recently been applied to make the S-I cycle more simplified and energy efficient. However, the performance of the electrochemical Bunsen reaction, especially the electrode reactions inside the electrolytic cell (EC) are not clear at present. In this work, a two-dimensional numerical model of EC was developed. The detailed reaction process was numerically calculated with considering the coupling of mass transfer and electrochemical reactions, and was verified using experimental data. The effects of various operating parameters on the reactions were investigated. The results showed that the increase of current density significantly improves the conversion rates of reactants. A higher temperature is unfavorable for concentrating H_2SO_4 and HI. Increase in the inlet flow rate reduces the conversion rates of reactants, but the impact declines with further rising flow rate. An optimal operating condition is also proposed. The theoretical simulation study will provide guidance for the improvement of experimental work.

Introduction

In recent years, the use of non-fossil fuels becomes imperative due to the great impact of fossil fuels on the earth's atmosphere temperature rise [1,2]. Hydrogen is considered to be an important new energy and sustainable energy, which reduces carbon dioxide and pollutant emissions while meeting global energy needs [3,4]. Over the past few decades, hydrogen-related technologies have developed rapidly and hydrogen utilization has become widespread [5]. Traditional ways for mass production of hydrogen are coal gasification, natural gas reforming and water electrolysis. Nevertheless, there is a growing development on renewable hydrogen production technologies [6,7]. Among them, sulfur–iodine (S-I) thermochemical water-splitting cycle, which usually associated with nuclear or solar energy, has been listed as one of the most promising large-scale and high-efficient hydrogen production processes [8,9]. The Japan Atomic Energy Agency (JAEA) achieved 8 h H_2 production with the rate of 10 L/h, and then designed a 100 L/h hydrogen demonstration project to verify the integrity of process components and hydrogen production

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Nomenclature

D	Diffusion coefficient ($m^2\ s^{-1}$)
E	standard electrode potential (V)
F	Faraday constant (96,487 C mol^{-1})
i	current density (A dm^{-2})
p	pressure (Pa)
T	temperature (K)
u	velocity vector (m s^{-1})
c	concentration (M)
R_i	reaction rate (mol $m^{-3}\ s^{-1}$)

Greek characters

σ	conductivity (S m^{-1})
φ	potential (V)
μ	viscosity (kg $m^{-1}\ s^{-1}$)
ρ	density (kg m^{-3})

stability [10]. Closed-cycle experiments of the iodine–sulfur process have been successfully conducted by the Institute of Nuclear and New Energy Technology of Tsinghua University (INET) in China, thereby confirming the feasibility and controllability of the process [11].

The S-I cycle mainly includes the following reactions [12]:

$$SO_2 + 2H_2O + I_2 \rightarrow H_2SO_4 + 2HI (293 \sim 393K) \quad (1)$$

$$H_2SO_4 \rightarrow SO_2 + H_2O + 0.5O_2 (1073 \sim 1273K) \quad (2)$$

$$2HI \rightarrow I_2 + H_2 (573 \sim 773K) \quad (3)$$

The overall reaction of the Bunsen reaction (1), the H_2SO_4 decomposition reaction (2) and the HI decomposition reaction (3) is the decomposition of water into hydrogen and oxygen, while SO_2 and I_2 are recovered and recycled as intermediates in the S-I cycle. The schematic is presented in Fig. 1. Bunsen reaction can occur spontaneously in the presence of excess water [13]. Since the reaction products can be dissolved in water, the separation of H_2SO_4 and HI is the focus of Bunsen reaction. GA first proposed the traditional method of using excess iodine [12]. The $H_2SO_4/HI/I_2/H_2O$ quaternary mixtures were spontaneously separated into two layers: H_2SO_4/H_2O in the upper sulfuric acid phase and $HI/I_2/H_2O$ in the hydroiodic acid phase [14]. However, the large amount of iodine and water dilute aqueous acids, in which impurities also exist. As a result, further separating, purifying, concentrating processes and recycling of excess material [15–17] before decomposition of H_2SO_4 and HI are inevitable. Thus, the general S-I processes are complicated and energy-intensive due to the application of traditional Bunsen reaction, which is detrimental to the development of S-I cycle.

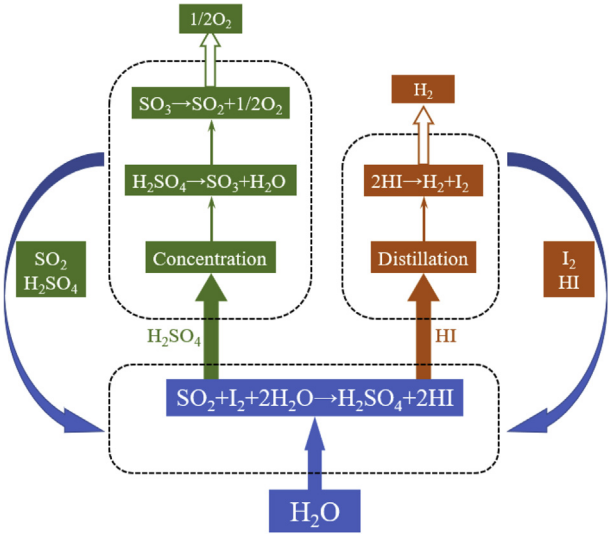

Fig. 1 – Schematic of S-I cycle for hydrogen production.

In order to overcome the shortcomings of the traditional Bunsen reaction, the new methods of Bunsen reaction have been proposed, including electrochemical technique, reaction in non-aqueous solvent and chemical precipitation [18–20]. Nomura et al. proposed to carry out the Bunsen reaction in an electrolytic cell [18]. A proton exchange membrane separates the anodic H_2SO_4 solution from the cathodic HI solution while allowing protons to be delivered from the anode to the cathode. The electrode reactions are shown in Eqs. (4) and (5):

$$Anode: SO_2 + 2H_2O - 2e^- \rightarrow H_2SO_4 + 2H^+ \quad (4)$$

$$Cathode: I_2 + 2H^+ + 2e^- \rightarrow 2HI \quad (5)$$

where SO_2 is oxidized at the anode and I_2 is reduced at the cathode during electrolysis. The concentrated H_2SO_4 and HI solutions are separated due to the proton exchange membrane in the electrolytic cell, resulting in the reduced excess I_2 and H_2O and less impurities in the two acids. Moreover, an over-azeotropic HI/H_2O solution can be produced in the cathode [21]. Therefore, the traditional liquid-liquid phase separation will be omitted [16], along with the simplification of the purification process since the impurities are negligible [20] and even the energy-intensive HI concentration processes, such as extractive distillation or electrodialysis [17]. And then the energy consumption of the new S-I cycle will be significantly reduced.

At present, most studies on the electrochemical Bunsen reaction mainly focus on its fundamental characteristics [18,20–27]. Compared to the traditional Bunsen reaction, the electrochemical Bunsen reaction can reduce 93% of excess iodine and 69% of excess water [18]. Immanuel et al. [22,23] studied the cell voltage–current characteristics at different temperatures, pressures and initial concentrations, along with the membrane properties. In our previous studies, the concentration of acids during electrolysis and the energy consumption were investigated [24]. The mass transfer, reaction and the impedance distribution in the EC were also determined based on the electrochemical characterization of electrodes [25]. Recently, the detailed kinetics of the electrochemical Bunsen reaction were studied using the polarization curve measurement [26]. The thermal efficiency of the new S-I cycle assembled with the electrochemical Bunsen reaction was calculated to be 42–50% and can be further improved [27].

Up to now, few work relates to the theoretical calculation of the electrochemical Bunsen reaction, which may be favorable for studying its internal reaction processes. To obtain a uniform distribution of flow, the optimal minimal pressure drop and electric power input, the performance of EC with five