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# Electrochemical investigation of the Bunsen reaction in the sulfur–iodine cycle

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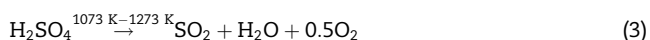
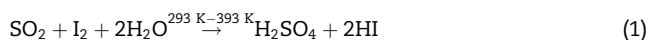
## ABSTRACT

The Bunsen reaction, as a part of the sulfur–iodine thermochemical cycle, was studied using an electrochemical cell. The effects of current density, operating temperature,  $\text{H}_2\text{SO}_4$  concentration in the anolyte, HI concentration and  $\text{I}_2/\text{HI}$  molar ratio in the catholyte were explored. Both the  $\text{H}_2\text{SO}_4$  in anolyte and the HI in catholyte were concentrated during electrolysis. Increasing current density amplified this  $\text{H}_2\text{SO}_4$  and HI concentration, while the other operating parameters also varied the anolyte and catholyte concentration. The transport properties of the cation exchange membrane were examined. The electrode current efficiency remained close to 100% for most runs except those at high current density. Both the average cell voltage and the heat equivalent of electric energy were determined at different conditions.

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## 1. Introduction

The sulfur–iodine (SI) thermochemical cycle, first proposed by General Atomics [1], is considered as one of the most promising routes for massive hydrogen production. The SI process consists of the Bunsen Reaction (1) and the hydriodic acid and sulfuric acid decomposition Reactions (2, 3), listed as follows:



Reaction (1), known as the Bunsen reaction, produces sulfuric acid (as an aqueous  $\text{H}_2\text{SO}_4$  solution) and hydriodic acid

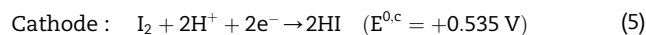
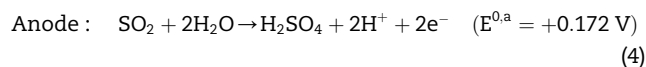
(as a HI solution). Both acids are purified, concentrated, and then decomposed into hydrogen and oxygen, as shown in Reactions (2) and (3). The traditional direct contact mode of the Bunsen reaction requires a large excess of both iodine and water with respect to their stoichiometric values [1]. The excess iodine induces a separation of the solution produced into two immiscible phases [2,3] and the excess of water makes the reaction thermodynamically more favorable [4]. One of the disadvantages of the traditional SI cycle is that a large amount of energy is required to remove the excess iodine and water before the decomposition of HI [5]; moreover the circulation of iodine in the whole cycle is undesirable, due to its corrosive characteristics. Therefore, the overall thermal efficiency of the SI cycle is greatly reduced.

In recent years, some alternative ways for carrying out the Bunsen reaction have been proposed in order to reduce the

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excess amounts of iodine and water [6]. The addition of a precipitating agent, such as lead sulfate, was proposed to remove iodide and thus induce separation of the two acids without the excess of iodine [6]. Reaction solvents, such as liquid SO<sub>2</sub>, tributylphosphate (TBP), ionic liquids, and molecular solvents, were used to extract the HI produced in the Bunsen reaction [6–9]; therefore, the presence of excess water can be avoided. Application of an electrochemical cell to the Bunsen reaction [10] is also a potential alternative. The electrolysis cell consists of two electrodes and two compartments separated by a cation exchange membrane. Gaseous SO<sub>2</sub> dissolved in H<sub>2</sub>SO<sub>4</sub> solution and solid iodine dissolved in HI solution is used as anolyte and catholyte, respectively. The reactions at the anode and cathode are:



This method offers several advantages: (1) the required amount of iodine and water is reduced and the liquid–liquid separator can be dropped; (2) it increases the concentration of H<sub>2</sub>SO<sub>4</sub> and HI simultaneously; (3) the recirculation of unreacted reactant is reduced in the overall process. Disadvantage of this electrochemical method is that it requires electric power for electrolysis.

The Bunsen reaction was studied by Nomura et al. in an electrochemical membrane reactor operated at room temperature [10]. Current–voltage characteristics were evaluated and this study showed that the total resistance between the electrodes was independent of the H<sub>2</sub>SO<sub>4</sub> concentration and decreased with declining I<sub>2</sub>/HI molar ratio. The overpotential at the anode was reduced by addition of a small amount of HI to the anolyte. In another experiment [11], conducted in a temperature range of 290–333 K, the resistance between the electrodes decreased with rising operating temperature, but it increased with rising H<sub>2</sub>SO<sub>4</sub> concentration. Thermal efficiency diminished with rising current density and H<sub>2</sub>SO<sub>4</sub> concentration. The same group [12] found that thermal efficiency grew with rising HI concentration and a maximum thermal efficiency of 38.9% was obtained.

In recent years, a group at the Indian Institute of Technology Delhi performed studies on the electrochemical Bunsen reaction. Cross-contamination through the membrane was measured [13] and showed that the electroosmotic flow induced by the current enlarged the concentration of sulfate ions and SO<sub>2</sub> in the catholyte and reduced the concentration of iodide ions in the anolyte. The same group characterized platinum and graphite electrodes using linear sweep voltammetry (LSV) and cyclic voltammetry (CV) [14]. Areal-resistance of the membrane was measured at different operating conditions [15]. Effects of anolyte pressure, catholyte pressure, temperature, H<sub>2</sub>SO<sub>4</sub> concentration in the anolyte, HI concentration and I<sub>2</sub>/HI molar ratio in the catholyte on cell voltage were investigated [16].

The concentration of HI and H<sub>2</sub>SO<sub>4</sub> is one of the important advantages for the electrochemical Bunsen reaction. Moreover, it is desirable to study the variation of anolyte and catholyte concentration during electrolysis at different

operating conditions. The transport properties of the cation exchange membrane strongly affect the cell performance, yet concrete data has not been reported in literature. In this work, the effects of current density, temperature, initial H<sub>2</sub>SO<sub>4</sub> concentration in the anolyte, initial HI concentration and I<sub>2</sub>/HI molar ratio in the catholyte on the evolution of anolyte and catholyte concentration were studied. Cell voltage was recorded during electrolysis. The transport properties of the membrane were determined, and for different runs the current efficiency and energy consumption during electrolysis were also calculated.

## 2. Experimental

### 2.1. Experimental setup

The Bunsen reaction was carried out in the experimental setup shown in Fig. 1. It mainly consists of an electrochemical cell, anolyte and catholyte reservoirs, the solution recirculation section between cell and reservoir, and a D.C. power supply. Fig. 2 shows a schematic diagram of the electrochemical cell (Hephas Energy Co., Ltd.), consisting of two graphite electrodes and a Nafion 117 membrane (DuPont Co., USA); the effective membrane area was 12.25 cm<sup>2</sup> (3.5 cm × 3.5 cm). Two rubber gaskets (170 μm thickness) were used at both sides of the membrane to prevent the intermixing of anolyte and catholyte. The temperature of the cell was controlled by means of a temperature controller (Hephas Energy Co., Ltd.). Two double-jacketed glass reservoirs operating at atmospheric pressure were placed on magnetic stirrers, and temperature was controlled using a thermostatic water bath (GX-2010, Shanghai Bilang Instrument Co.). Teflon tubes were employed to connect the reservoirs with each compartment of the cell. Two peristaltic pumps (BT100-2J, Baoding Longer Precision Pump Co., Ltd.) were used for circulating the solutions. In order to avoid heat dissipation, the teflon tubes were wrapped with heat insulation cotton. A D.C. power supply (PAN16-10A, KIKUSUI ELECTRONICS CORP., Japan) provided a constant current to the cell and monitored the cell voltage.

### 2.2. Electrolysis

Table 1 lists the operating conditions for the electrochemical Bunsen reaction. The total amount of water (the sum of water in the acids and the extra feed water) was fixed at 50 g for both anolyte and catholyte. The anolyte reservoir was initially filled with known amounts of sulfuric acid (about 98 wt. %, Quzhou Juhua reagent Co., Ltd.) and deionized water, while the catholyte reservoir was filled with known amounts of hydriodic acid (approximately 56 wt%, Shanghai Kefeng Industrial Co., Ltd.), iodine (>99.9%, Chinasun Specialty Products Co., Ltd.) and deionized water. Both solutions were recirculated through their respective loops by two peristaltic pumps, the flow rate of both anolyte and catholyte was fixed at 10 ml/min. To start the test, the stirrer, the thermostatic water bath, and the temperature controller were switched on. After the system had reached the desired temperature, gaseous SO<sub>2</sub> was continuously fed at a constant flow rate of 20 ml/min into the H<sub>2</sub>SO<sub>4</sub> solution of the anolyte reservoir. This bubbling

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