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# Direct electrolysis of Bunsen reaction product HI/H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O/toluene mixture for hydrogen production: Pt electrode characterization

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## ABSTRACT

In chemical cycles to produce hydrogen, the H<sub>2</sub>S splitting cycle and the sulfur-iodine (S–I) water splitting cycle both share the Bunsen reaction and HI decomposition. Therefore, they have to overcome the same challenges in the technology development, one of them being the complex and difficult separations of the mixed hydroiodic acid and sulfuric acid solution after the Bunsen reaction. To avoid the separations, this paper studies the electrolysis of the HI/H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O/toluene mixture, focusing on the electrochemical characterization of the Pt electrode by using linear sweep voltammetry (LSV) and cyclic voltammetry (CV). The results show that hydrogen is identified from the gas generated from the cathode in electrolysis. Iodide oxidation is the main reaction in the anode chamber and no significant side reactions are observed. Iodine deposition on the anode surface increases the resistance to iodide diffusion to the anode. However, it can be mitigated by adding toluene in or applying stirring to the anolyte HI/H<sub>2</sub>SO<sub>4</sub> solution. The Pt cathode and sulfuric acid catholyte also work stably.

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## Introduction

Hydrogen is not only a clean energy carrier but also an important commodity especially in fuel and fertilizer production [1]. Nowadays, hydrogen is mainly produced by hydrocarbon reforming processes where greenhouse gas, carbon dioxide, is emitted. Attempts have been made to develop clean and economical technologies for hydrogen production.

Among them, the thermochemical sulfur-iodine (S–I) water splitting cycle is considered one of the most promising potential technologies for large-scale hydrogen production. The production can become even greener when coupled with nuclear, hydro or solar energy sources.

In the 1980s, the sulfur-iodine (S–I) cycle was firstly proposed by General Atomics [2]. It consists of three chemical reactions [3]:

Bunsen reaction

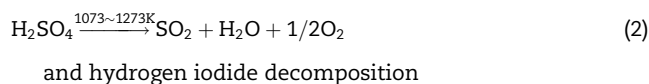
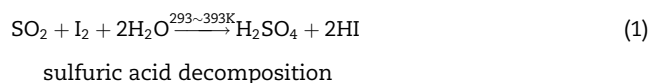
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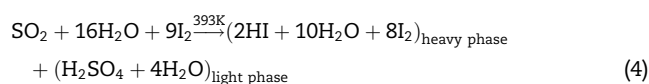
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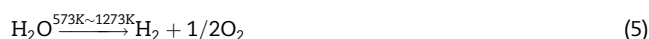
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The Bunsen reaction produces  $\text{H}_2\text{SO}_4$  and HI mixed acid which is difficult for direct separation. But the two acids can form two immiscible liquid phases at a particular stoichiometry of excessive iodine and water, where each stays in one phase [3–5]:

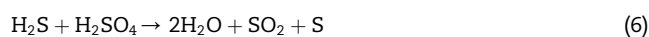


After the subsequent concentration and purification, sulfuric acid ( $\text{H}_2\text{SO}_4$ ) is sent for reaction (2) and HI is sent for reaction (3) where  $\text{H}_2$  is formed. When  $\text{I}_2$  returns to the Bunsen reaction, the water splitting cycle is completed and the net reaction becomes



Based on extensive studies in the feasibility and optimization of  $\text{H}_2\text{S}$  removal using sulfuric acid [6–10] and the inspiration of thermochemical S–I cycle, Wang [11] proposed a novel  $\text{H}_2\text{S}$  splitting cycle to convert  $\text{H}_2\text{S}$ , an industrial waste, into  $\text{H}_2$  and  $\text{H}_2\text{SO}_4$  via the following reactions:

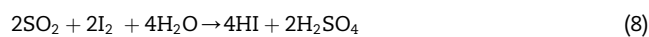
$\text{H}_2\text{S}$  oxidation



S oxidation



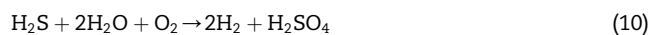
Bunsen reaction



HI decomposition



The overall reaction is:

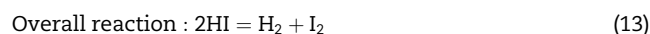


The  $\text{H}_2\text{S}$  splitting cycle provides chemical route to not only recover sulfur or convert sulfur to sulfuric acid but also recover hydrogen from one of the major industrial wastes in oil upgrading and refining, hydrogen sulfide, which is now mainly handled by sulfur removal and recovery based on the Claus process. The technical feasibility of the  $\text{H}_2\text{S}$  splitting cycle has been investigated, and this route for hydrogen production could be carbon free when coupling with nuclear power plants [11]. The upper boundary thermal efficiency of the  $\text{H}_2\text{S}$  splitting cycle was higher than that of the S–I cycle because of the higher internal energy that  $\text{H}_2\text{S}$  has [12]. Because the reactions between hydrogen sulfide and sulfuric acid have been studied by Wang and coworkers and the oxidation of sulfur to  $\text{SO}_2$  is a commercially-available

technology, to engineer this new  $\text{H}_2\text{S}$  splitting cycle for hydrogen production, the challenges are still focused on those found for the Bunsen reaction and the HI decomposition. To overcome the challenges, efforts have been made to optimize the stoichiometry of reactants, enhance the separation characteristics of HI and  $\text{H}_2\text{SO}_4$  mixture, and avoid side reactions [4,5,13–25]. The reverse reaction of the Bunsen reaction ( $\text{H}_2\text{SO}_4 + 2\text{HI} \rightarrow \text{SO}_2 + \text{I}_2 + 2\text{H}_2\text{O}$ ) is used to purify HI and  $\text{H}_2\text{SO}_4$  [26–28]. New methods to operate the Bunsen reaction include the electrochemical method, the precipitation method, and the non-aqueous solvent method. Conducting the Bunsen reaction in an electrochemical membrane reactor can reduce the consumption of iodine and avoid the direct separation of the HI/ $\text{H}_2\text{SO}_4$  mixture [29–38]. Adding precipitants such as lead sulphate to remove HI can avoid the concentration of HI and prevent side reactions between HI and  $\text{H}_2\text{SO}_4$  [39]. Using the organic solvent or the ionic liquid to carry out the Bunsen reaction greatly decreases the consumption of iodine and water, resulting in reduction of the corrosion from the HI- $\text{H}_2\text{O}$  azeotropic mixture, and the improvement of the system thermal efficiency [40–45]. These alternative methods have their advantages, but they come into new problems that need further study. Moreover, the subsequent HI decomposition from a dilute solution still begins with the energy-intensive purification and concentration, and the decomposition itself is also energy-intensive.

Wang [46] proposed dissolving iodine in toluene and conducting the Bunsen reaction at room temperature or lower temperatures than the melting point of iodine. The low-temperature Bunsen reaction can avoid side reactions, reduce the deposition of iodine vapor, and lessen severe corrosion potentials. In toluene solvent, the solubility of  $\text{I}_2$  and  $\text{SO}_2$  is relative high, on the contrary, the solubility of  $\text{H}_2\text{SO}_4$  and HI is extremely low. The use of toluene can efficiently separate the products and unreacted reactants of the Bunsen reaction and reduce the excessive use of iodine and water [46]. The apparent reaction rate of the Bunsen reaction in the presence of toluene was investigated with a gas-liquid-liquid multiphase system [47]. It indicated that the reaction rate was the first order with respect to  $\text{SO}_2$  and  $\text{I}_2$  and the rate-determining step was the mass transfer of  $\text{SO}_2$  from gas phase to liquid phase. Wang et al. also proposed to directly send the products from the Bunsen reaction including hydroiodic acid, sulfuric acid, water, and toluene for electrolysis where HI is converted to hydrogen and iodine [47].

The electrochemical reactions are shown as follows:



Iodide is oxidized to iodine at anode with the anolyte of HI,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}$ , and toluene. Hydrogen is generated at the cathode with sulfuric acid as catholyte which has higher conductivity than water. If complete conversion of iodide is achieved, this process can avoid the direct separation of hydroiodic acid from sulfuric acid, one of the bottlenecks that hinder the technology development.

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