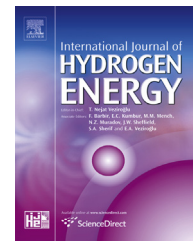




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Equilibrium potential for the electrochemical Bunsen reaction in the sulfur–iodine cycle

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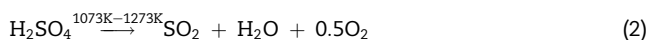
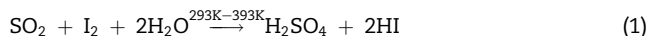
ABSTRACT

The electrochemical Bunsen reaction was carried out in an electrochemical cell, where the anodic and cathodic compartments were separated by a Nafion 117 membrane. The equilibrium potential of the cell was experimentally measured and theoretically modeled. The effect of electrolyte concentration and temperature was explored. An increase in SO₂ or I₂ concentration reduced the equilibrium potential, whereas increasing H₂SO₄ or HI concentration had a contrary effect. The cell equilibrium potential decreased with increasing temperature. The derived theoretical equilibrium potential model was verified by the experimental data. The regression parameters M and Z in the model were independent of electrolyte concentration, but M decreased and Z kept constant with increasing temperature. An empirical equilibrium potential formula was proposed based on the theoretical and experimental results. The good reproducibility of this formula for measured data indicated its feasibility to estimate the equilibrium potential and also its guidance for optimizing the electrochemical Bunsen reaction.

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Introduction

Hydrogen production via sulfur–iodine (SI) thermochemical water-splitting cycle [1] has been considered a high efficient and promising technique, and has been studied extensively for more than 30 years. The SI cycle relates to three main reactions, as seen below:



Reaction (1) among SO₂, I₂, and H₂O is known as the Bunsen reaction, which produces H₂SO₄ and HI for the following decomposition reactions (2) and (3). The total reaction is the splitting of water into H₂ and O₂, while SO₂ and I₂ are recycled. The required highest temperature of the SI cycle is only ~1123 K. Solar or nuclear energy can be used for heat supply. Meanwhile, this cycle is a clean method for hydrogen production without CO₂ emission and has a high thermal efficiency of 40–50% [2].

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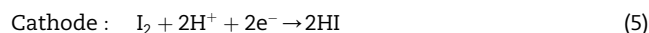
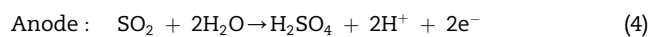
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For the Bunsen reaction, the separation of two acids is the biggest challenge because H_2SO_4 and HI are miscible. Up to now, the most common method to overcome this problem is using excess iodine with respect to its stoichiometric value [1]. The complexation between iodide and excess iodine forms polyiodide [3], and then increases the density of HI solution. As a result, the H_2SO_4 and HI spontaneously separated due to the density difference. Moreover, the excess water is required to dilute H_2SO_4 and HI so as to obtain a negative Gibbs free energy and make the Bunsen reaction thermodynamically more favorable. The 4–6 mol excess iodine and 11–13 mol excess water at the temperature of 330–350 K have been proposed as an optimal operating window for the Bunsen reaction [4]. The large excess amounts of iodine and water lead to many disadvantages in the cycle [5–7], including the occurrence of side reactions between two acids, the requirement of a liquid–liquid separator, the purification of H_2SO_4 and HI solutions, concentration of HI solution before decomposition, and iodine transportation. Therefore, the thermal efficiency of the SI cycle can be reduced as the above processes consume a large amount of energy.

To overcome the difficulties in the traditional Bunsen reaction, some innovative techniques, including the addition of precipitating agent, solvents, and electrochemical method, have been proposed for the time being [8]. Among them, the electrochemical Bunsen reaction not only reduces the excess iodine and water, but also eliminates the traditional liquid–liquid separator and purification process [9]. The Bunsen reaction is carried out using an electrochemical cell, where the anolyte ($\text{SO}_2\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$ solution) and catholyte ($\text{I}_2\text{--HI--H}_2\text{O}$ solution) are separated by a cation exchange membrane. The anode and cathode reactions are then driven when the electric current is supplied.



The performance of the electrochemical Bunsen reaction has been studied in recent years [9–17]. The amount of iodine was reduced by 93% compared with the traditional Bunsen reaction. The cell voltage was found to change with the electrolysis at a constant current, and the cell resistance decreased with rising temperature. Application of this technique to the SI cycle led to a thermal efficiency of 42.1% [10]. The effects of anolyte/catholyte concentration, pressure, and temperature on the voltage–current characteristics have been determined [15]. And in our earlier works [16,17], the detailed process of electrolysis have been analyzed, and some results concerning the concentration of acids, the energy consumption, the transport properties of membrane, and the cross-contamination between two electrolytes, have been obtained.

The electric energy is required for the electrolysis, which is the main disadvantage of the electrochemical Bunsen reaction. Therefore, it is important to optimize the energy consumption because it affects the total thermal efficiency of the SI cycle. The consumed electric energy is dominated by the cell voltage and current efficiency. The current efficiency usually relates to the transport properties of the membrane, i.e., the permeability of protons and water through the membrane. The cell voltage mainly consists of the

equilibrium potential (or the open circuit voltage), the electrode overpotential, the potential drop resulting from the ohmic resistance offered by anolyte, catholyte, and membrane, and the potential drop to overcome the mass transfer or the diffusion resistance. Evaluation on the electrode overpotential and the ohmic potential drop as a function of current density for the electrochemical Bunsen reaction has been conducted [15]. The equilibrium potential, which is independent of current density but relating to the operating conditions, affects a lot on the cell voltage but has less been reported.

In this work, the equilibrium potential for the electrochemical Bunsen reaction was evaluated based on the experimental measurement and theoretical modeling. The effect of electrolyte concentration and temperature on the equilibrium potential was explored. The theoretical equilibrium potential model was deduced and verified by the experimental data. An empirical formula for the equilibrium potential was proposed based on the experimental and theoretical results.

Experimental

Fig. 1 shows the experimental setup used for measuring the equilibrium potential. It mainly consists of an electrochemical cell, anolyte and catholyte reservoirs, and a Potentiostat/Galvanostat. The cell has a 5 cm × 5 cm Nafion 117 membrane and two graphite electrodes. A temperature controller was used to adjust the cell temperature. The two double-jacketed glass reservoirs were connected to anodic and cathodic compartment of the cell using Teflon tubes and peristaltic pumps. The temperature of the reservoirs was controlled by a thermostatic water bath. A Potentiostat/Galvanostat was employed to measure the equilibrium potential for the electrochemical Bunsen reaction.

The known amounts of commercial sulfuric acid (~98 wt %) and deionized water were filled in the anolyte reservoir, SO_2 was fed into the H_2SO_4 solution at a flow rate of 20 ml/min. The catholyte reservoir was filled with commercial hydriodic acid (~56 wt%), iodine (>99.9%), and deionized water. To keep the correlation with our previous work [16], the base case was chosen as 10 mol/kg_{H₂O} H_2SO_4 and 1.07 mol/kg_{H₂O} SO_2 in the anolyte, 6 mol/kg_{H₂O} HI and 0.5 I₂/HI molar ratio in the catholyte, and 323 K temperature. The concentration of anolyte, catholyte, and the cell temperature were changed to determine their effects on the equilibrium potential. The molar fraction of H_2SO_4 and SO_2 in the anolyte was in a range of 0.14–0.22 and 0.008–0.047, while the HI and I₂ molar fraction in the catholyte was 0.09–0.12 and 0.02–0.08, respectively. The system was operated at 303, 323, 333 and 343 K. To minimize the errors results from instrument, three repetitive measurements were taken at each condition.

Theoretical modeling

The distribution of the equilibrium potential (E_0) in an electrochemical cell for the Bunsen reaction is shown in Fig. 2. It

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