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Electrochemical characterization of electrodes in the electrochemical Bunsen reaction of the sulfur–iodine cycle

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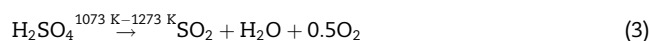
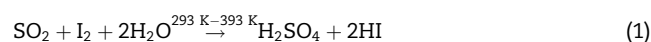
ABSTRACT

In the electrochemical Bunsen reaction, SO_2 is oxidized to H_2SO_4 at the anode while I_2 is reduced to HI at the cathode. Both electrodes were electrochemically characterized using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The effects of H_2SO_4 concentration in the anolyte, as well as HI concentration and I_2/HI molar ratio in the catholyte, were explored. The cyclic voltammograms of platinum electrode shift with rising scan rate, indicating the irreversibility of two electrode reactions. The equivalent circuit for the cathode reaction impedance consists of an ohmic resistance of the solution, in series with a parallel combination of a charge transfer resistor and a constant phase element, yet the impedance spectra for the anode reaction can be modeled using a parallel combination of a charge transfer resistor and a constant phase element. The electrode reaction kinetics was also analyzed using the exchange current density (j_0) and the standard reaction rate constant (k^0). The results indicate that a high electrode reaction rate in the cell can be obtained for a HI concentration of 8 mol/kg_{H₂O} and an I_2/HI molar ratio of 0.5 in the catholyte and a H_2SO_4 concentration of 13 mol/kg_{H₂O} in the anolyte.

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1. Introduction

The sulfur–iodine (SI) thermochemical cycle proposed by General Atomics in the 1980s [1], is considered as one of the most promising and efficient among the various thermochemical methods for hydrogen production. The SI cycle consists of three reactions:



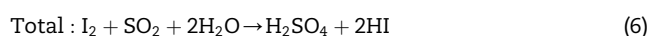
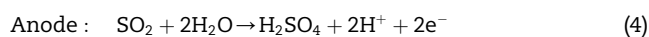
The Bunsen reaction (1) produces two immiscible phases, a H_2SO_4 phase ($\text{H}_2\text{SO}_4\text{--H}_2\text{O}$) and a HIx phase ($\text{HI--I}_2\text{--H}_2\text{O}$), using an excess amount of iodine and water with respect to their stoichiometric values [1]. The complexation reaction between I_2 and I^- increases the density of the HIx phase and rejects

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H_2SO_4 and H_2O , leading to separation of the two phases [2–4]; excess water dilutes the concentration of H_2SO_4 and HI, which makes the reaction thermodynamically more favorable [5]. The two phases obtained are purified, concentrated, and then decomposed into H_2 and O_2 (Reactions (2 and 3)). The other products, such as I_2 , SO_2 , and H_2O , are recycled back to the Bunsen reaction, so that the only raw material in this closed cycle is water, while the products are H_2 and O_2 .

The main disadvantage of the SI cycle is that a large amount of excess iodine and water is required, which reduces the overall thermal efficiency [6]; yet many efforts have been made to improve the Bunsen reaction. One of the alternatives is the application of an electrochemical cell [7]. Gaseous SO_2 dissolved in a H_2SO_4 solution and solid iodine dissolved in a HI solution are used as anolyte and catholyte, respectively, and filled in a two-compartment cell separated by a cation exchange membrane and two electrodes. The H_2SO_4 and HI are produced in respective compartments:



This electrochemical method has several advantages: (a) it reduces the excess amount of iodine and water, for example, the amount of excess iodine by 93% and the amount of water by 69% [8]; (b) it allows to eliminate a liquid–liquid separator and thereby reduces the capital cost by ~20% [7]; (c) the electrolysis concentrates simultaneously both H_2SO_4 and HI [7].

Fundamental research on the electrochemical Bunsen reaction has been related [7–14]. The electrolysis of Bunsen reaction performed by Nomura et al. showed that the cell voltage changed with electrolysis [7] and the total cell resistance decreased with rising temperature [8]. Nomura et al. [9] also explored the effects of operating parameters on the total thermal efficiency of the SI cycle using this electrochemical method. The maximum thermal efficiency of 38.9% is obtained and the I_2/HI molar ratio could be reduced to 0.5 without decreasing the thermal efficiency. The cross-contamination between the anolyte and catholyte due to the permeation of unexpected solutes through the membrane has been measured by Immanuel et al. [11,12]. The same group studied the cell voltage–current characteristics at different pressures, temperatures, H_2SO_4 concentrations, HI concentrations, and I_2/HI molar ratios [13]. They also characterized the platinum and graphite electrodes using linear sweep voltammetry and cyclic voltammetry [10], yet the effects of the H_2SO_4 or HI concentration on the electrode reactions have not been investigated. In our previous work, the evolution of anolyte and catholyte concentration during electrolysis and the transport properties of the membrane were studied, and for different conditions the current efficiency and energy consumption were determined [14].

The electrochemical characterization of the anode and cathode in the electrolysis cell is one of the key performance indicators for the electrochemical Bunsen reaction. However, less has been reported on this aspect. It is desirable to identify the reversibility of electrode reactions and determine the

effects of solution concentrations on the electrode reactions using cyclic voltammetry. Moreover, since electric power is required for the electrolysis, it is necessary to study the various electric resistances for the electrode reactions in order to determine the transport processes at electrodes and electrode reaction kinetics at different solution concentrations. Electrochemical impedance spectroscopy is one of the most powerful means to characterize the resistances of the cell, e.g., the charge transfer resistance, the ohmic resistance of solution and membrane, etc. Already EIS has been employed in various fields of electrochemistry [15–18], and it can be used to study electrode reaction kinetics as well [19–21].

In this work, an electrochemical characterization of anode and cathode in the electrochemical Bunsen reaction was accomplished using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The effects of the H_2SO_4 concentration in the anolyte, the HI concentration and the I_2/HI molar ratio in the catholyte were explored. The electrode reaction kinetics was also investigated in terms of EIS analysis.

2. Experimental

To study the anode and cathode reactions respectively, that is to measure only one half of the electrolysis cell for the electrochemical Bunsen reaction, a three-electrode cell comprising of a working-, a counter-, and a reference-electrode was chosen for the CV and EIS measurement of anode and cathode reactions, as shown in Fig. 1. Working electrode is the designation for the electrode being studied, thus its selection is crucial. In most electrochemical experiments, this is often an inert material, commonly gold, platinum or carbon. A platinum wire was chosen as the working electrode for CV and EIS tests, considering its high conductivity, good stability, and low cost. Counter electrode is the electrode that pairs with a working electrode and completes the current path. In a three-electrode cell, the potential changes of the working electrode were independent of

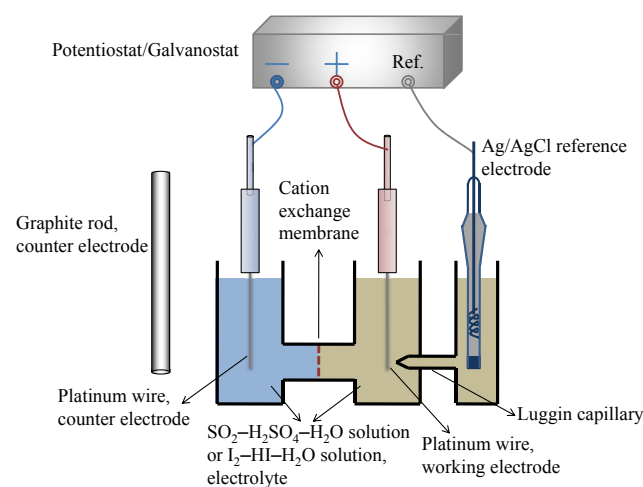


Fig. 1 – Schematic diagram of a three-electrode setup used for cyclic voltammetry and electrochemical impedance spectroscopy measurement.

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