

Investigation of Using Sulfur-Containing Gases in Low-Temperature Fuel Cell at Sulfuric Acid Production Site

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Abstract

The possibility and effectiveness of using sulfur dioxide and hydrogen sulfide as the fuel in low-temperature fuel cells at the sulfuric acid production site has been investigated. A fuel cell has been designed and constructed using palladium as a catalyst, which enables conversion of the energy of oxidation of sulfur dioxide and hydrogen sulfide to the electric energy. The experimental data showed that the use of hydrogen sulfide and sulfur dioxide as a fuel allows achieving the power of 1.0 and 0.5 mW, respectively. The comparative studies with the use of hydrogen in the same fuel cell resulted in the power of about 2.0 mW, i.e. the use of hydrogen sulfide delivers a performance comparable with that of the hydrogen. The processes of oxidizing of the sulfur containing gases are used in our company in production of sulfuric acid. Oxidation of these gases conducted using the conventional technological processes. The use of these processes to produce energy as a byproduct could be an attractive way to reduce the energy consumption of the whole process. Considering the relatively high power obtained in this work for the sulfur containing gases fed fuel cells, the substitution of conventional oxidation of sulfur containing gases in this technological chain by the fuel cell oxidation, and by-producing the electric energy, could be very profitable for the energy efficiency enhancement of the main production process. In the future work, the design and development of fuel cell catalysts and membranes to enhance the performances of sulfur containing fuel cells will be significant.

Introduction

The global environmental issues and the energy crisis demand for the alternative sources of energy and its efficient and sustainable use. Therefore, among the other means of energy sources, the development of fuel cells [FCs] for primary and auxiliary power for stationary, portable, and automotive systems have been rapidly accelerated. FCs are the electrochemical devices which directly convert the energy of oxidation of various fuels into electric energy. FCs is a not new concept, and was reported in 19th century by a British scientist W.R. Grove [1]. It took long time this technology to mature and become a commercial technology to produce the electricity. Nowadays, due to the high conversion efficiency, FCs have become one of the most promising power sources for various applications [2].

Different organic and inorganic compounds can be used as fuels for FCs. Hydrogen-oxygen fuel cell

is well developed. The final product of the cell reaction is water, electricity, and heat, which are environmentally friendly. But hydrogen-oxygen fuel cells suffer from high cost of hydrogen, safety and storage problems [3, 4]. A recent comprehensive review of fuel cell activity is given in the literature [5, 6].

The sulfur-containing gases could be used as fuel for the FCs based on the oxidation process according to the equation



Furthermore, the large amounts of sulfur-containing gases (such as H₂S and SO₂) are produced worldwide every year, mainly as by-products from petroleum, natural gas and coal gasification industries. It should be noted that sulfur-containing gases are cheap and considered as wastes and air pollutants. Several technologies and methods have been

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developed to remove sulfur-containing gases, such as adsorption, absorption, hydrogen production and two-step Clause process. Removal process usually is expensive. In our company, these gases are oxidized to produce sulfuric acid. Conducting such oxidation process in fuel cell to produce the electricity to at least partially cover the plant operation needs in electricity could be favorable to reduce the final product cost.

Thus, the development of the devices for the electrochemical oxidation/conversion of these gases with simultaneous power generation could provide potentially economical and powerful energy sources [7-10]. There are some applications of such systems as use of sulfur dioxide in Li-SO₂ batteries for space applications [11], and use of sulfur dioxide in the gas electrochemical cells [12]. Hydrogen sulfide is widely investigated in high-temperature fuel cells as well [2, 4, 13-17].

Several patents were published on the H₂S electrochemical oxidation at low temperatures in the range between 25-165 °C and low-pressure range from 0.14 – 0.41 MPa [18, 19]. A platinum-carbon or MoS₂-carbon composite anode was used in this case, while the cathode was a platinum-carbon composite. A solid proton-conducting membrane Nafion and polybenzimidazole was used as a separator between cathode and anode. The reaction conversion of H₂S has reached about 100%, and the output voltage of 500 mV has been achieved even at a high loading of more than 10 kOhm.

In this work, the sulfur-containing gases (H₂S and SO₂) used in the sulfuric acid production were studied as fuel for low-temperature FCs with the atmospheric oxygen as the oxidizer; the electrochemical performance of these cells were investigated and compared with the hydrogen fed FCs.

Experimental

Figure 1 schematically shows a stable working fuel cell designed and constructed in this work using palladium as a catalyst, which enables the oxidation of sulfur dioxide and hydrogen sulfide by oxygen. On the anode side: the fuel (H₂S or SO₂ in water or H₂) are supplied through an inlet pipe 10, where they first go through the channels in a Teflon plate 1 and a graphite current collector plate 2 and delivered to the palladium catalyst 3. Extra fuel and the oxidation products are removed through the outlet tube 11. On the cathode side: air is supplied through an entrance pipe 8, passes through the channels in a Teflon plate 1 and graphite current collectors 2, and finally reaches the carbon cloth 4 where activated by palladium. Extra air accompanied with water is removed through the outlet pipe 9. The effective area of electrodes was 3.6 cm².

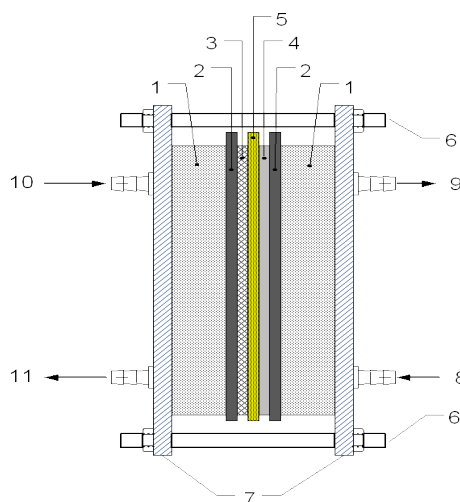


Fig. 1. Fuel cell with the palladium catalyst: 1 – Teflon plates; 2 – current collectors (graphite plates); 3, 4 – catalyst (palladium); 5 – Nafion (proton exchange membrane); 6 – bolts, 7 – endplates, 8 – supply of air (by compressor); 9 – outlet of excess air and reaction products; 10 – supply of fuel; 11 – outlet of excess fuel and reaction products.

The cell voltage and current were measured by a galvanostat/potentiostat VMP3 (BioLogic, USA), an ionometric converter “Aquilon I-500”, and digital multimeters. Hydrogen sulfide was obtained by heating a mixture of sulfur-paraffin-asbestos; hydrogen was produced by electrolysis of water; and sulfur dioxide was prepared by the reaction of sodium sulfide with sulfuric acid. Sulfur dioxide was used in the experiments as a 10% aqueous solution. Heated air was supplied to the FC using an air compressor.

Results and Discussions

Sulfur Dioxide as Fuel

The oxidation of sulfur dioxide can take place in a weak acidic, neutral and alkaline media. Typically, in the neutral environment, it follows the reaction below:



The reaction can be described as a sequence of two steps: at first, SO₂ is oxidized to SO₃, and further SO₃ dissolves in water and forms H₂SO₄. The second step is not a RedOx reaction. Hence, the electromotive force (EMF) calculated based only on the first step of the reaction as follows



Theoretical EMF equation:

$$E = \Delta G / (n * F) = 70900 / (2 * 96500) = 0.37 \text{ V} \quad (4)$$

Where F is the Faraday's constant; n is the number of electrons involved in the reaction.

Figure 2 shows the cell voltage and current dependence on the operation temperature obtained during the oxidation of sulfur dioxide. Initially, the cell temperature was increased from 55 °C ("x" indicates the beginning of the steps, Fig. 2a) to 61 °C, then gradually decreased to 40 °C. In the third step, it was increased to 50 °C again to investigate the temperature performance of the cell. From Fig. 2a, it can be seen that at the resistance/load of 75 Ohm, the current and voltage decreased when the temperature increased from 56 °C to 61 °C. While during the second step, the voltage and current gradually increased during the decrease of temperature

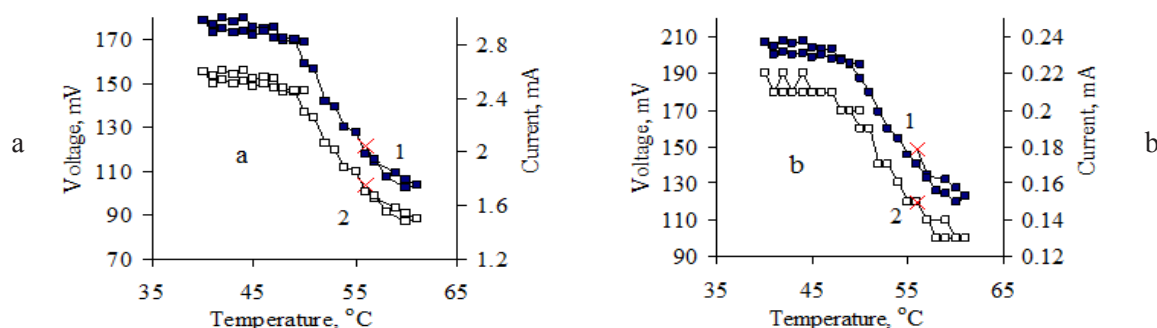


Fig. 2. Temperature dependence of (1) cell voltage and (2) current during the oxidation of SO_2 at different current loads: (a) 75 Ohm and (b) 1075 Ohm. The "x" indicates the beginning of the process.

from 61 °C to 51 °C. Interestingly, the voltage and current stopped increasing and kept constant the temperature dropped to 51 °C and further to 40 °C. After reaching 40 °C, even though the temperature increased to 51 °C, similar voltage and current trends were obtained. The highest output power at 75 Ohm was about 0.45-0.47 mW between 40-47 °C. The power has drastically decreased to 0.15 mW when the temperature increased to 61 °C. In the same time, at a high resistance of 1075 Ohm, similar voltage and current curves were obtained. Even though the output voltage (190-205 mV) was higher than that in the low resistance load (170-180 mV), the current was 10 times less, which resulted in low output power.

The theoretical EMF oxidation value of SO_3^{2-} to SO_4^{2-} is 0.79 V. However, in water system, SO_2 first dissolves in the molecular state rather than in the ionized form. Therefore, the EMF value could be considered as that of the oxidation of dissolved SO_2 molecules into SO_3^{2-} , and equal 0.37 V. The higher voltage at low temperature could be due to an increase of SO_3^{2-} ions concentration at lower temperature in the SO_2 aqueous solution.

Hydrogen Sulfide as Fuel

Several different reactions could be expected when the hydrogen sulfide is oxidized. When it is oxidized to sulfuric acid, the theoretical EMF is -0.85 V. This value is equal 1.06 V if H_2S is transformed to sulfur. The EMF of sulfur oxidation to sulfur dioxide is 0.78 V, and 0.64 V if further oxidized to sulfur trioxide. The total cell voltage could be calculated using these values.

Figure 3 shows the cell voltage and current dependencies on the working temperature obtained during the oxidation of hydrogen sulfide. The experiments were performed at the temperatures from 65

to 105 °C. Same steps were conducted as in the case of the sulfur dioxide oxidation. From Fig. 3a, at the resistance of 75 Ohm, the maximum voltage (230-260 mV) and current (3.4-3.8 mA) values were observed at two different temperature ranges, 67-76 °C and 92-99 °C, respectively. A sharp maximum was observed at the elevated temperatures. When the temperature is reduced to 104 °C, two maximums were observed, the first of them is in the lower temperature region. The corresponding maximum power was around 1 mW (shown in Fig. 5a).

At the load of 1075 Ohm, the voltage is higher for about 60 mV and the maximum voltage of 290 mV could be reached; however, the current and power were found to be lesser (Fig. 3b). For the load of 5 Ohm in the temperature range of 71-75 °C the voltage is 80-77 mV and the current is 17.2-16.7 mA with the power reaching 1.4 mW.

The differences in the temperature dependences of the current, voltage and power could be explained by the stepwise oxidation of hydrogen sulfide. The electrochemical reactions products are water, sulfur, sulfur dioxide and sulfuric acid.

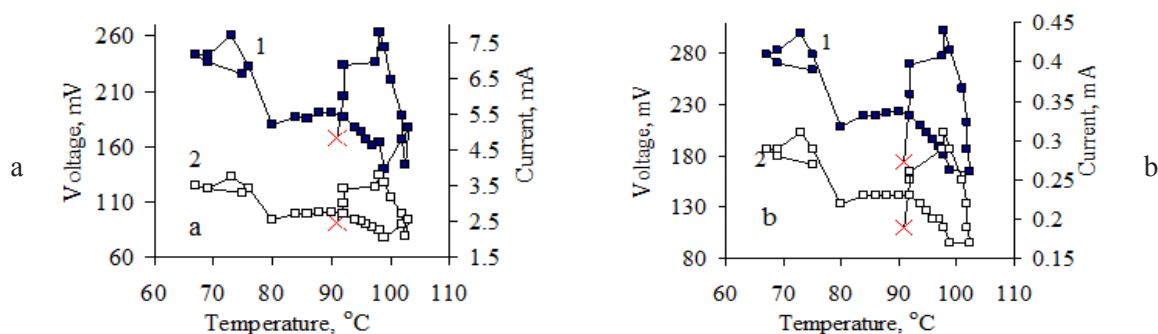


Fig. 3. Temperature dependence of (1) cell voltage and (2) current during the oxidation of H_2S under different current loads: (a) 75 Ohm and (b) 1075 Ohm. The “x” indicates the beginning of the process.

Hydrogen as Fuel

For comparison purposes, hydrogen was also studied as fuel in our experiments. The results are shown in Fig. 4. As shown in Fig. 4a, the fuel cell operated stably between 60-90 °C without drastically drop in voltage and current at a lower loads. The output voltage and current were 370 mV and 5.4 mA, respectively. At the load of 1075 Ohm, the similar trends were observed as shown in Fig. 4b. Although the voltage was found to be

50% higher compared with that at lower load, the cell current is only 0.6 mA, i.e. nine times less.

The output power at different temperatures during the oxidation process is shown in Fig. 5.

As shown in Fig. 5a, at a low load, hydrogen could produce around 2 mW between 60-90 °C while in the case of hydrogen sulfide this value could reach 1 mW between 70-100 °C; the sulfur dioxide use as a fuel allows achieving the power of the cell about 0.5 mW around 40 °C.

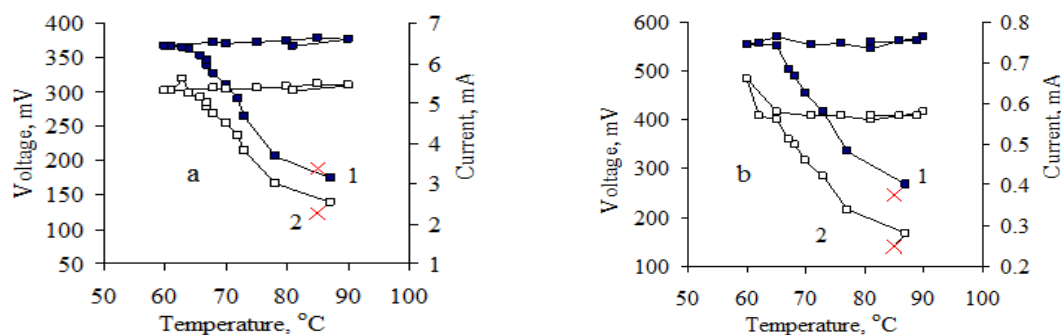


Fig. 4. Temperature dependence of (1) cell voltage and (2) current during the oxidation of H_2 under different current loads: (a) 75 Ohm and (b) 1075 Ohm. The “x” indicates the beginning of the process.

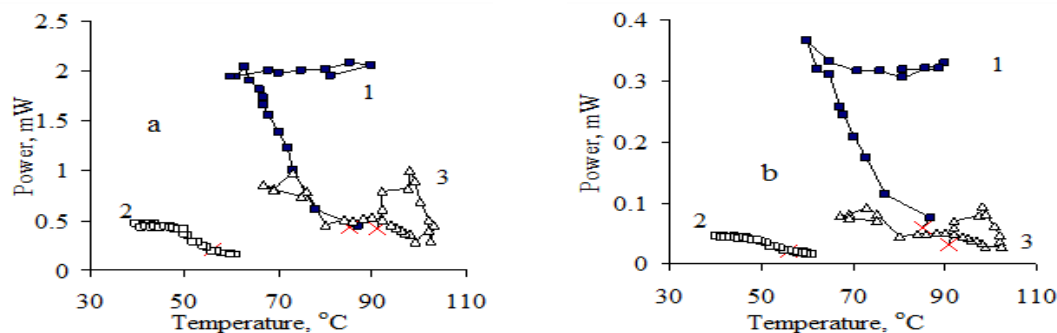


Fig 5. Temperature dependence of the power under different current loads: (a) 75 Ohm and (b) 1075 Ohm. Fuels: 1 – hydrogen, 2 – sulfur dioxide, 3 – hydrogen sulfide. The “x” indicates the beginning of the process.

Conclusions

The possibility and effectiveness of use of sulfur dioxide and hydrogen sulfide as “the fuel” in the low-temperature fuel cells with the atmospheric oxygen as oxidizer at the sulfuric acid production site have been studied. The output power of 2.0, 1.0 and 0.5 mW were achieved when hydrogen, hydrogen sulfide and sulfur dioxide were used as fuels, respectively. This shows that hydrogen sulfide oxidation could be used as an industrial process to produce sulfuric acid and sulfur and to obtain the electricity. Using this process to produce electricity in a fuel cell as by-product at the sulfuric acid production site could be profitable considering a relatively high power obtained in this work to enhance the energy efficiency of the major production process. In the future work, design and development of fuel cell catalysts and membranes to enhance the performances of sulfur containing FCs are significant.

Acknowledgements

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