Novel Composite Hydrogen-Permeable Membranes for Non-Thermal Plasma Reactors for the Decomposition of Hydrogen Sulfide

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Abstract

The goal of this experimental project is to design and fabricate a reactor and membrane test cell to dissociate hydrogen sulfide (H_2S) in a non-thermal plasma and recover hydrogen (H_2) through a superpermeable multi-layer membrane. Superpermeability of hydrogen atoms (H) has been reported by some researchers using membranes made of Group V transition metals (niobium, tantalum, vanadium, and their alloys), although it has yet to be confirmed in this study.

A pulsed corona discharge (PCD) reactor has been fabricated and used to dissociate H_2S into hydrogen and sulfur. A nonthermal plasma cannot be produced in pure H_2S with our reactor geometry, even at discharge voltages of up to 30 kV, because of the high dielectric strength of pure H_2S (~ 2.9 times higher than air). Therefore, H_2S was diluted in another gas with lower breakdown voltage (or dielectric strength). Breakdown voltages of H_2S in four balance gases (Ar, He, N_2 and H_2) have been measured at different H_2S concentrations and pressures. Breakdown voltages are proportional to the partial pressure of H_2S and the balance gas. H_2S conversion and the reaction energy efficiency depend on the balance gas and H_2S inlet concentrations. With increasing H_2S concentrations, H_2S conversion initially increases, reaches a maximum, and then decreases. H_2S conversion in atomic balance gases, such as Ar and He, is more efficient than that in diatomic balance gases, such as N_2 and H_2 . These observations can be explained by the proposed reaction mechanism of H_2S dissociation in different balance gases. The results show that nonthermal plasmas are effective for dissociating H_2S into hydrogen and sulfur.

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Introduction

Gas streams containing hydrogen sulfide (H_2S) are encountered in almost all fossil fuel energy extraction and processing systems. The conventional treatment method for H_2S is the Claus process, which produces sulfur and water by the net reaction: $\text{H}_2\text{S} + \text{O}_2 \rightarrow \text{S} + \text{H}_2\text{O}$. The reaction is inefficient because the valuable potential product hydrogen (H_2) is converted into water. The transformation of hydrogen in a weakly bound state in H_2S to a strongly bound state in H_2O results in the loss of a potential H_2 source. Hydrogen sulfide would have a much higher economic value if both sulfur and chemical hydrogen could be recovered instead of just sulfur. Therefore, direct dissociation of H_2S into H_2 and sulfur would be preferable.

Many methods have been investigated to dissociate H_2S into its constituent elements, including thermal decomposition (either catalytic or noncatalytic), electrochemical methods, photochemical methods, and plasma methods.¹ Compared to electrochemical methods and photochemical methods, thermal decomposition and plasma decomposition are promising methods because of relatively low energy consumption.² However, the thermal decomposition reaction of H_2S is endothermic with low equilibrium conversions even at high temperatures.³ For example, thermal decomposition of H_2S has an equilibrium conversion of 12% at 1 atmosphere pressure and 1000°C. At temperatures less than 550°C, the thermal equilibrium conversion of H_2S is less than 1%. Therefore, two methods are proposed to overcome the thermodynamic limitation of H_2S conversion. One is product removal by condensation of the sulfur and separation of the hydrogen with membranes (see Zaman and Chakma¹, and references therein). The other is to create a nonthermal equilibrium environment for H_2S

conversion, for instance, in a nonthermal plasma. Nonthermal plasma technologies are characterized by low gas temperature and high electron temperature because high energy electrons are produced in the gas while the bulk temperature of the gas is unchanged. A nonthermal plasma is a partially ionized gas that provides a source of chemically active species, including radicals, excited states and ions, that can promote chemical reactions at ambient temperatures. Therefore, nonthermal plasmas overcome the disadvantage of high temperature because the majority of the electrical energy goes into the production of energetic electrons rather than into gas heating. For reactions that are thermodynamically unfavorable and for which low equilibrium conversions are obtained at high reaction temperatures, nonthermal plasmas have an advantage over thermal processes because thermal equilibrium is not achieved.

Direct dissociation of H₂S has been investigated using various plasma processing technologies, including arc discharge (thermal plasma), microwave plasma, glow discharge, silent discharge, and pulsed corona discharge. Dalaine et al.^{4, 5} investigated H₂S conversion in gas systems with 0-100 ppm H₂S in air using gliding arc discharges. This type of reactor is rather inefficient, with an energy consumption of 500 eV/H₂S. The theoretical minimum energy requirement for the decomposition of H₂S is over three orders of magnitude less than this (for H₂S(g) → H₂(g) + S(s), ΔH₂₉₈ = 0.21 eV/H₂S, 1 eV/molecule = 96.5 kJ/mol). A large amount of work on microwave decomposition of H₂S has been carried out in the former Soviet Union,⁶⁻¹¹ where both laboratory and pilot units were reportedly used for the decomposition of pure H₂S alone or H₂S/CO₂ mixtures with a very low energy consumption of about 0.76 eV/H₂S. Encouraged by the high conversions and low energy requirements claimed by the Russian researchers, a joint

project for H₂S conversion using microwave plasmas was undertaken by The Alberta Hydrogen Research Program, Atomic Energy of Canada, and Shell Canada Limited. Unfortunately, this group reported the energy consumption for H₂S conversion to be about 4.5 eV/H₂S² and thus was unable to reproduce the low energy consumption reported by the Russian researchers. All microwave plasma experiments on H₂S conversion were performed at pressures below 1 atmosphere, which implies higher energy consumption for compression and vacuum costs. Traus et al.^{12, 13} investigated 10-100% H₂S conversion in Ar, N₂, and H₂ in a silent discharge reactor and a rotating glow discharge reactor. They concluded that the energy consumption of H₂S conversion in a rotating glow discharge reactor (~ 27 eV/H₂S) is less than that in a silent discharge reactor (~ 81 eV/H₂S). In addition, Abolentsev et al.¹⁴ and Ma et al.¹⁵ investigated decomposition of low (ppm) concentrations of H₂S in different balance gases including air, N₂, H₂, He, and CH₄ using a silent discharge reactor. H₂S conversion in pulsed corona discharge reactors was also investigated by several investigators.¹⁶⁻¹⁹ These investigations were conducted at low H₂S concentrations (<2%) and the energy consumption of H₂S conversion was high (>100 eV/H₂S), which are not practical for commercial application.

Despite this extensive research on H₂S conversion, many questions remain unanswered. First, all of the research described above has been done either below atmospheric pressure or at low H₂S concentrations (<2%). H₂S conversion at pressures above atmospheric and at high H₂S concentrations is desirable in order to determine if the plasma method has potential for industrial application. Second, there are no reports on the breakdown voltage of H₂S at pressures higher than atmospheric and H₂S

concentrations >2%. Breakdown voltage data are very important because they provide references for experimental operating conditions, such as charge voltage and gas pressure. H₂S is an electronegative gas with a high dielectric strength of about 2.9²⁰ (The loss of the dielectric properties of a gas as a result of application of an electric field greater than a certain critical magnitude is called a dielectric field. The critical magnitude of the electric field or the voltage at which the breakdown of a gas takes place is called the dielectric strength of the gas or breakdown voltage.²¹) The common gases like air, N₂, H₂, and the noble gases have very low dielectric strengths of 1, 1, 0.5, and 0.15-0.18, respectively.²¹ Therefore, much higher breakdown voltages are required for electrical breakdown of H₂S compared to these gases in the same reactor geometry. In addition, electrons are accelerated over the mean free path of gas molecules in the process of electrical breakdown. The mean free path of gas molecules increases with decreasing gas pressure. Hence, electrons obtain more energy at low gas pressures under the same operating conditions,²² which means that the breakdown voltage of a gas decreases with decreasing gas pressure. Therefore, the electrical breakdown of H₂S at either low pressures or low H₂S concentrations in a balance gas with a low dielectric strength is comparatively easy. However, electrical breakdown of H₂S at pressures above atmospheric and at high H₂S concentrations is more difficult. Third, the mechanism of H₂S conversion in the plasma is not clear. Since the ionization potential of H₂S (10.4 eV) is considerably lower than He (24.6 eV), Ar (15.8 eV), N₂ (15.6 eV), H₂ (15.4 eV), CH₄ (12.6 eV), O₂ (12.1 eV), and H₂O (12.6 eV),²¹ Ma et al.¹⁵ and Helfrich¹⁶ proposed that the conversion of H₂S is through the ionization ($e + \text{H}_2\text{S} \rightarrow \text{H}_2\text{S}^+ + 2e$) and subsequent charge neutralization ($\text{H}_2\text{S}^+ + e \rightarrow \text{HS} + \text{H}$). Abolentsev et al.¹⁴ presented another

mechanism of H₂S conversion, (1) the balance gas (M) is ionized to M⁺, (2) H₂S⁺ is formed by charge transfer reaction (M⁺ + H₂S → M + H₂S⁺), and (3) H₂S is dissociated by reaction with an ionized H₂S molecule (H₂S⁺ + H₂S → H₃S⁺ + HS). Traus et al.^{12, 13} proposed that radicals, such as H and HS, formed in the plasma are responsible for H₂S conversion. In fact, the ionization degree in nonthermal plasma is quite low. A recent investigation by Zhao et al.²³ showed that ionization reactions in nonthermal plasmas are negligible.

Therefore, the goals of this work are to investigate the breakdown voltage and conversion mechanism of H₂S in four balance gases (Ar, He, N₂, and H₂) in a pulsed corona discharge reactor (PCDR) at pressures above atmospheric and at high H₂S concentrations (≥4%). A PCDR was chosen to investigate H₂S conversion because (1) PCD plasmas have been extensively investigated and used in methane conversion²⁴ and NO_x decomposition²⁵⁻²⁸ and (2) comparison of energy efficiency of methane conversion in three kinds of nonthermal plasma reactors (PCD, microwave, and silent discharge) shows that PCD reactors are one to two orders of magnitude more energy efficient than the other two.²⁹

Executive Summary

Hydrogen sulfide (H_2S) is a potential resource for the production of molecular hydrogen (H_2) that is currently being lost because the established industrial Claus process converts H_2S into water and elemental sulfur. This project seeks to recover H_2 from H_2S by combining plasma reactor processing with multi-layer membranes to efficiently dissociate H_2S and recover the H_2 in a pure form.

The project has six main tasks: staffing, procurement of equipment and supplies, membrane fabrication, permeation cell fabrication, membrane evaluation, and reports and briefings. Staffing the project has been completed. Procurement of equipment and supplies, membrane fabrication, membrane evaluation, and the reporting tasks are all ongoing.

An experimental reactor and permeation cell has been fabricated and used extensively for methane decomposition experiments, the details of which were included in the previous annual report. Based on experience with this test cell, an improved reactor was constructed that permits visual observation of the corona and more accurate temperature measurements along the axial length of the reactor. This report contains results from H_2S decomposition experiments obtained during the second project year. The H_2S was diluted with four different gases (helium, argon, nitrogen, and H_2) because the breakdown voltage of pure H_2S is too high to form a plasma in pure H_2S streams with the present reactor geometry. The minimum charge voltages required to establish a corona in each of these four gas mixtures has been established. This data has provided mechanistic insight on the decomposition of H_2S in plasmas that suggests that direct electron collision with H_2S and excitation of balance gas molecules followed by subsequent reaction with H_2S are the dominant reaction pathways. The energy efficiency for the H_2S decomposition is the best that has been reported at reaction conditions that are above atmospheric pressures and $>2\%$ H_2S concentrations. The efficiency is better than all previous reports, including those at sub-atmospheric pressures and low H_2S concentrations, with the exception of some low pressure, low concentration microwave plasmas. However, the efficiency is still ~ 80 times lower than the theoretical limit. Although improvements in reactor design should increase efficiency, proper operation of the hydrogen separation membranes will be required in order to achieve efficiencies that will make this technology practical for industrial application.

Superpermeability, or plasma driven permeation, of atomic hydrogen has not yet been demonstrated during the project. By analogy with literature reports on the active species in NO_x decomposition plasmas, the active H atoms may exist in significant concentrations only very near (within a few millimeters) of the reactor anode. The anode is approximately 12 mm away from the membrane in the present reactor design, which makes it improbable that the H atoms can reach the membrane surface before combining to form molecular H_2 , which has very low permeability at the near ambient temperatures in the reactor. Both niobium and platinum coated stainless steel membranes have been evaluated for hydrogen permeability, but neither exhibited superpermeability. A third type of membrane, a porous ceramic support with vanadium deposited in the pores by

chemical vapor deposition (known as Type 3 in the project proposal), is being fabricated to test one more membrane type. In the meantime, a third reactor is being designed that will combine the anode with the hydrogen membrane and thus place the membrane in close proximity to the source of the active species. The project is slightly behind schedule with regard to membrane development and testing, as the Type 3 membranes should have been fabricated during the last quarter, but the more significant issue at this time is to complete construction of the new reactor.

One paper has been submitted to a peer-reviewed journal and this report will be the basis for a second paper.

Experimental

Figure 1 shows a diagram of the experimental system. The system consists of a reactor with an electrical system built around a thyatron switch, a flow control and distribution system, and a gas sampling system. The reactor is oriented vertically, with the gas flow from bottom to top. The electrical system can deliver charge voltages from 6.9 kV to 30 kV at pulse frequencies from 0 to 1000 Hz. The capacitor bank provides space for four doorknob capacitors in increments of 640 pF. The thyatron switch element is cooled with compressed air. The capacitors are charged to the desired voltage using a 40 kV oil-cooled high voltage power supply. On triggering the thyatron, the stored energy in the capacitors is discharged in a few nanoseconds to the anode, giving rise to a high rate of change of voltage (dv/dt) on the anode. This process of charging and discharging the capacitors is repeated based on the thyatron trigger frequency leading to sustained current streamers or plasma. Electrical breakdown that initiates

Figure 1. Experimental setup

1. H₂S gas cylinder. 2. balance gas cylinder (Ar, He, N₂, H₂). 3. mass flow controller. 4. pressure gauge. 5. pulsed corona discharge reactor. 6. sulfur condenser. 7. valve. 8. RGA. 9. data collection computer. 10. thyatron switch. 11. HV power supply and control circuit. 12. discharge waveform recorder.

corona discharge can be detected by a discharge waveform recorder. The cathode was a stainless steel tube with 0.024 m in diameter and 0.914 m in length, while the anode was a stainless steel wire 0.001 m in diameter passing axially through the center of the tube. The wire was positively charged, while the tube was grounded. The gas flowing through the reactor tube was converted to plasma by the high voltage discharge from the reactor anode.

The four gas mixtures of H₂S in Ar, H₂S in He, H₂S in N₂, and H₂S in H₂ are prepared by mixing ultra high pure (UHP) H₂S and the UHP balance gas. Gas mixtures flow through PCDR at the entrance conditions of ambient temperature (~300K) and the set pressure. The highest pressure used in this work is 5.0 bar. The desired entrance mole fraction of H₂S is achieved by setting flowrates of H₂S and the balance gas using two well-calibrated mass flow controllers. The energy released by the capacitors per pulse was calculated from $\frac{1}{2}CV_c^2$, where C is the pulse forming capacitance, fixed at 1920 PF in this work, and V_c is the constant charge voltage before discharge. The power consumed, W (J·s⁻¹), was calculated as the product of the input energy per pulse and the pulse frequency, $\frac{1}{2}fCV_c^2$, where f is pulse frequency in Hz. The analysis of the gas leaving the sulfur condenser was carried out by means of an online Residual Gas Analyzer (RGA, Stanford Research Systems, Inc. QMS100), which is a mass spectrometer with a quadrupole probe. To perform quantitative measurements, an internal standard method³⁰ was used to calibrate the ion signal response at an m/z ratio of 34 with the H₂S mole fraction, in which balance gas was used as an internal standard. The calibration results are shown in Figure 2.

Figure 2. Calibration plot for H₂S relative to an internal standard (balance gas).

The plots in Figure 2 consist of the ratio of the corresponding quantities versus the ratio of instrument response for H₂S and balance gas, which show very good linear relationship

$$\frac{y_{H_2S}}{y_B} = a \cdot \frac{I_{H_2S}}{I_B} + b \quad (1)$$

where y is the mole fraction of gas, I is the ion current from RGA, and the subscript B represents the balance gas of Ar, He, N₂, of H₂. Therefore, the measured ion current ratio of H₂S and the balance gas can be used to determine the mole fraction ratio of H₂S and the balance gas (K) from Figure 2. For a binary gas mixture at the reactor entrance, the mole fraction of H₂S and the balance gas can be calculated from

$$y_{i,H_2S} = \frac{K_i}{K_i + 1} \quad (2)$$

$$y_{i,B} = \frac{1}{K_i + 1} \quad (3)$$

where the subscript i represents the inlet gas. When the corona discharge is on, H₂S is dissociated into H₂ and sulfur. For the balance gases Ar, He, and N₂, the effluent gas mixture is the ternary system (sulfur is captured by a sulfur condenser). However, the mole fraction of balance gas at the reactor outlet is the same as that at the reactor inlet because the reaction of H₂S dissociation is an equimolar gas phase reaction when the sulfur product is condensed. The outlet H₂S mole fraction can be determined from

$$y_{o,H_2S} = K_o \cdot y_{i,B} \quad (4)$$

where the subscript o represents the outlet gas. For the balance gas H₂, the outlet H₂S mole fraction is

$$y_{o,H_2S} = \frac{K_o}{K_o + 1} \quad (5)$$

Therefore, the conversion of H₂S in the PCDR is calculated from

$$X_{H_2S} = \frac{y_{i,H_2S} - y_{o,H_2S}}{y_{i,H_2S}} \quad (6)$$

Conversion rate and energy consumption of H₂S conversion are calculated from

$$r = \frac{PF}{RT} \cdot y_{i,H_2S} \cdot X_{H_2S} \text{ (mol} \cdot \text{s}^{-1}\text{)} \quad (7)$$

$$En = \frac{W}{r} \cdot 1.0364 \times 10^{-5} \text{ (eV} \cdot \text{molecule}^{-1}\text{)} \quad (8)$$

where P is the gas pressure, F is the gas flowrate, T is the temperature, and R is the gas constant.

For each parameter set, at least two experiments were performed to assure that the results are repeatable. All experimental data were reproducible within a $\pm 10\%$ error limit, including the RGA and flow measurement uncertainties.

Results and Discussion

Breakdown voltage of H₂S in several balance gases. Gas breakdown voltage depends on the specific reactor configuration, especially the electrode configuration and structure. The breakdown voltage of many pure gases has been investigated in both uniform and non-uniform fields.³¹ For uniform fields, the breakdown voltage usually follows Paschen's law, which states that breakdown voltage, V_b , is a function of nd only, n being the gas density and d is the distance between the electrodes. For non-uniform fields, the breakdown voltage is a function of nr , where r is the radius of curvature of the electrode surface at the point where the highest value of the electric field strength occurs.³¹ For the PCD reactor used in this work, r is the radius of wire anode. For many pure gases in non-uniform fields, the breakdown voltage was found to be proportional to nr at pressures higher than 0.5 bar.³¹

Gas breakdown can be detected by the discharge waveform recorder, as shown in Figure 1. In addition, if corona discharge occurs, the discharge noise from PCDR can also be clearly heard. At low charge voltages, no discharge occurs. Experimentally, the charge voltage is increased in increments of 0.1 kV until the discharge is observed from both the discharge waveform recorder and the noise from the reactor. The measured breakdown voltages at different pressures for pure Ar, H₂, and N₂ are shown in Figure 3. For our reactor, the anode radius, r , and temperature are 0.0005 m and 300 K, respectively. Therefore, nr is proportional to gas pressure. The results presented in Figure 3 show that breakdown voltage is proportional to gas pressure, which is consistent with previous reports.³¹ Breakdown voltages of pure N₂

measured at flowrates of $1.18 \times 10^{-4} \text{ SCM}\cdot\text{s}^{-1}$ and $7.87 \times 10^{-6} \text{ SCM}\cdot\text{s}^{-1}$ are almost the same, as shown in Figure 3, which indicates no effect of gas flowrate on breakdown voltage. In addition, pulse frequencies above 300 Hz do not affect breakdown voltage.

Figure 3. Breakdown voltage of pure gas as a function of pressure.
 (■): Ar at $1.18 \times 10^{-4} \text{ SCM}\cdot\text{s}^{-1}$ and 400 Hz; (●): H₂ at $1.18 \times 10^{-4} \text{ SCM}\cdot\text{s}^{-1}$ and 400 Hz;
 (▲): N₂ at $1.18 \times 10^{-4} \text{ SCM}\cdot\text{s}^{-1}$ and 400 Hz; (▼): N₂ at $7.87 \times 10^{-6} \text{ SCM}\cdot\text{s}^{-1}$ and 400 Hz

Breakdown of pure He occurs at any pressure from 0.8 to 5.0 bar gauge at the lowest charge voltage of 6.9 kV used in this work. However, breakdown of pure H₂S does not occur at pressures from 0.8 to 5.0 bar gauge and charge voltages from 6.9 to 30 kV, the entire operation range for our reactor. These results and results in Figure 3 indicate that the order of breakdown voltage at constant pressure is: He < Ar < H₂ < N₂ < H₂S, which is consistent with the order of increasing dielectric strength of these gases^{20, 21} (dielectric strength, He: 0.15, Ar: 0.18, H₂: 0.50, N₂: 1.0, H₂S: 2.9). Helium has the lowest breakdown voltage while H₂S has the highest.

Because no corona is formed in pure H₂S at the maximum charge voltage (30 kV) with our reactor configuration, H₂S must be mixed with another gas with low dielectric strength in order to initiate electrical discharge. He, Ar, N₂, and H₂ are used as balance gases in this work because no additional byproducts are produced in the corona.

Because both gas flowrate and pulse frequency (>300 Hz) do not affect breakdown voltage, gas breakdown experiments are carried out at a fixed gas flowrate of 1.18×10^{-4} SCM·s⁻¹ and a pulse frequency of 400 Hz. Figure 4 shows the breakdown voltage of H₂S in H₂. At each fixed H₂S concentration, the breakdown voltage is proportional to total gas pressure as shown in Figure 4 (a).

$$V_b = m_i \cdot P_t + n_i \quad (9)$$

where P_t is the total gas pressure in bar, m_i and n_i are the slope and the intercept at a specific H₂S mole fraction, respectively. Figure 4 (b) shows the slope m_i and the intercept n_i as a function of H₂S mole fraction. These results show that the slope m_i is proportional to H₂S mole fraction and the intercept n_i is essentially constant. Therefore Equation (9) can be rewritten as

$$V_b = (a_1 \cdot y_{H_2S} + b_1) \cdot P_t + n = a_1 \cdot P_{H_2S} + b_1 \cdot (P_{H_2S} + P_{H_2}) + n \quad (10)$$

where a_1 and b_1 are the slope and the intercept of linear relationship of m_i and H₂S mole fraction, respectively, P_{H_2S} and P_{H_2} are the partial pressure of H₂S and H₂, respectively. Equation 10 can be further simplified as

$$V_b = a_2 \cdot P_{H_2S} + b_2 \cdot P_{H_2} + c \quad (0.8 \text{ bar} < P_t < 3.6 \text{ bar}) \quad (11)$$

where $a_2 = a_1 + b_1$, $b_2 = b_1$, and $c = n$. Equation (11) indicates that breakdown voltage is proportional to partial pressures of the components in binary gas mixtures.

Figure 4. Breakdown voltage of H₂S in H₂: (a) Breakdown voltage as a function of total gas pressure. Experimental data: (□): 4% H₂S, (○): 8% H₂S, (△): 12% H₂S, (▽): 16% H₂S, (+): 25% H₂S; linear regression: (—): 4% H₂S, (---): 8% H₂S, (···): 12% H₂S, (– · –): 16% H₂S, (---): 25% H₂S. (b) Slope and intercept of liner regression in (a) as a function of H₂S mole fraction. (■): slope m_i ; (▲): intercept n_i .

Application of Equation (11) to mixtures of H₂S in Ar, H₂S in He, H₂S in N₂, and H₂S in H₂, parameters a_2 , b_2 , and c are obtained through a least-square regression analysis. The breakdown voltages (V_b) are,

$$\text{H}_2\text{S in Ar: } V_b \text{ (kV)} = 22.2 \times P_{\text{H}_2\text{S}} \text{ (bar)} + 2.52 \times P_{\text{Ar}} \text{ (bar)} + 6.48 \quad (12a)$$

$$\text{H}_2\text{S in He: } V_b \text{ (kV)} = 16.2 \times P_{\text{H}_2\text{S}} \text{ (bar)} + 2.42 \times P_{\text{He}} \text{ (bar)} + 3.35 \quad (12b)$$

$$\text{H}_2\text{S in N}_2: V_b \text{ (kV)} = 16.1 \times P_{\text{H}_2\text{S}} \text{ (bar)} + 6.44 \times P_{\text{N}_2} \text{ (bar)} + 4.00 \quad (12c)$$

$$\text{H}_2\text{S in H}_2: V_b \text{ (kV)} = 15.2 \times P_{\text{H}_2\text{S}} \text{ (bar)} + 4.74 \times P_{\text{H}_2} \text{ (bar)} + 2.70 \quad (12d)$$

Figure 5 shows the experimental results and the fitted data using Equation 12 (a)-(d). Most experimental data matched the fitted data very well, except experimental data for low concentrations (<4%) of H₂S in Ar. In this exceptional case, an increase in gas pressure causes the breakdown voltage to pass through a maximum, fall to a minimum, and then increase. Similar experimental phenomena are also observed for 2% H₂S in Ar. The reason for this exception is not clear yet.

Figure 5. Breakdown voltage as a function of total gas pressure. (a) H_2S in Ar; (b) H_2S in He; (c) H_2S in N_2 ; (d) H_2S in H_2
 Experimental data: ($\square$): 4% H_2S ; ($\circ$): 8% H_2S ; ($\triangle$): 12% H_2S ; (∇): 16% H_2S ; ($\diamond$): 20% H_2S ; (+): 25% H_2S ; ($\times$): 30% H_2S .
 Calculated data: (—): 4% H_2S ; (— —): 8% H_2S ; ($\cdots$): 12% H_2S ; ($-\cdot-\cdot-$): 16% H_2S ; ($-\cdots-$): 20% H_2S ; (---): 25% H_2S ; ($-\cdot\cdot-$): 30% H_2S .

H_2S conversion in several balance gases. Experiments on H_2S conversion in Ar, He, N_2 , and H_2 are carried out at fixed pulsed frequency of 400 Hz, charge voltage of 17 kV (corresponding to power input of 110 W), reactor pressure of 1.34 bar, and gas flowrate of $1.18 \times 10^{-4} \text{ SCM}\cdot\text{s}^{-1}$, corresponding to gas residence time of 4.25 s in the reactor. As shown in Figure 5, the charge voltage of 17 kV is higher than all breakdown voltages for gas mixture of H_2S in

Ar, H₂S in He, H₂S in N₂, and H₂S in H₂ at total pressure of 1.34 bar, which confirmed that electrical discharges occur for H₂S conversion.

Figures 6(a)-(d) show conversion and rate data for H₂S as a function of initial H₂S mole fraction. Similar trends of conversion and rate of H₂S for gas mixtures of H₂S in Ar, H₂S in He, H₂S in N₂, and H₂S in H₂ are found. Conversion of H₂S decreases with increasing H₂S mole fraction, while the rate initially increases, reaches a maximum, and then decreases with increasing H₂S mole fraction.

Figure 6. Conversion and conversion rate of H₂S as a function of H₂S mole fraction in several balance gases: (□): conversion; (■): conversion rate.

There are four proposed pathways to initiate H₂S conversion in nonthermal plasmas.

(I) Direct ionization of H₂S followed by dissociative recombination^{15, 16}:

(II) Ionization of the balance gas (M), leading to the charge transfer reaction, and the subsequent dissociative recombination reaction¹⁴:

(III) Direct electron collision dissociation of H₂S:

(IV) Electron collision dissociation or/and excitation of balance gas. These active species then contribute to H₂S dissociation:

Pathways (I) and (II) are unlikely for H₂S conversion for the following reasons:

(1) If pathway (I) is responsible for H₂S conversion, more H₂S molecules can be ionized with increasing H₂S concentration, which should lead to increasing H₂S conversion rates with increasing H₂S concentration. This effect is not observed, as shown in Figure 6.

(2) If pathway (II) is responsible for H₂S conversion, then the ionization energies of the balance gases should be reasonably achieved within the reactor. However, this is not the case, as shown by the following example using He, which has an ionization energy of 24.6 eV/He or 2370 kJ/mol He. At 110 W power input, if the whole energy input is assumed to be absorbed by He to form He⁺, the limiting conversion rate of H₂S is 46.3 μmol/s. However, the results

presented in Figure 6(b) show that most H₂S conversion rates are larger than 46.3 μmol/s, which leaves pathway II unable to explain all of the observed H₂S conversion.

(3) As shown in our recent investigation,²³ the degree of ionization in the pulsed corona discharge is low. The major active species are produced through electron collision in the streamers, whose total volume is 10^{-4} - 10^{-3} of the reactor volume.³² In the streamer head, the concentration of ions (corresponding to concentration of electrons) is around 15 ppm.²³ If pathways (I) and (II) are responsible for H₂S conversion and all ions formed from reactions R1 and R3 contribute to H₂S conversion, the conversion of H₂S for initial mole fractions of 0.04 is $400 \text{ Hz} \times 4.25 \text{ s} \times 15 \text{ ppm} \times (10^{-4}\text{-}10^{-3}) / 0.04 = 0.064\text{-}0.0064\%$, which is at least two orders of magnitude lower than conversion of H₂S observed during the experiments, as shown in Figure 6. Therefore, H₂S conversion through ionic reactions is unlikely if not impossible.

Conversion of H₂S through pathways (III) and (IV) can be supported by the following points.

(1) As demonstrated by Eliasson and Kogelschatz,^{33, 34} in the streamer head, the concentration of radicals and excited states formed from electron collision reactions are at least two orders of magnitude higher than that of ions. In the streamer channel, the concentration of radicals and excited states formed from electron collision reactions is at least four orders of magnitude higher than that of ions. Most reactions are known to occur in the streamer channel.²³ Therefore, if reactions R5-R7 contribute to H₂S conversion, the conversion of H₂S for initial mole fractions of 0.04 is $400 \text{ Hz} \times 4.25 \text{ s} \times (10^4 \times 15 \text{ ppm}) \times (10^{-4} \sim 10^{-3}) / 0.04 = \sim 64\%$, which is higher than all the experimental results shown in Figure 6. This is understandable because the efficiency of such a plasma reaction is less than 100%.

(2) The occurrence of H₂S conversion through direct electron collision reaction R5 can be demonstrated by the experimental data of H₂S conversion in He. The main active species formed from electron collision reaction with He are excited states. The first electronic excited state of He, He(2³S₁), has an excitation energy of 19.82 eV.³⁵ If the excited states of He were the only active species contributing to H₂S (R6 and R7), the highest conversion rate of H₂S in He is 110 W/(19.82 × 96.5 kJ/mol) = 57.5 μmol/s. However, for concentrations of H₂S in He less than 12%, the conversion rates of H₂S are higher than 57.5 μmol/s, which indicates that direct electron collision reaction of H₂S (R5) must also contribute to H₂S conversion in addition to the He excited states.

The observed maximum in H₂S conversion rate in Ar, He, N₂, and H₂ with increasing mole fraction of H₂S can be explained through pathways (III) and (IV). For H₂S in Ar, previous investigation³⁶ has shown that the major product for direct electron collisions with Ar is the lowest excited state of Ar, Ar(³P₂), which has an excitation energy of 11.55 eV.

Ar(³P₂) contributes to H₂S dissociation and H₂ dissociation as follows^{37, 38}:

Similarly, the following reactions contribute to H₂S conversion for H₂S in He³⁹⁻⁴¹:

There are no reports of rate constants for reactions R12 and R13.

For H₂S in N₂, the major products of electron collision reactions with N₂ are N radicals and N₂(A) (the first electronic excited state of N₂).⁴²

Previous investigation²² has shown that rate of electron collision reaction R15 is about 7 times higher than that of R14. These active species react with N₂, H₂S, and H₂,⁴³⁻⁴⁵ as follows:

There are no reports of reaction of H₂S and N. However, by analogy with the extremely low rate constant for the reaction of N with H₂O ($4 \times 10^3 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ at 1073 K),⁴⁶ we presume that N does not contribute to H₂S conversion and that N radicals predominantly recombine to N₂ because rate constant of R17 is about 8×10^6 higher than that of R16. In addition, no nitrogen containing byproducts such as ammonia were detected, which confirms that the only products of H₂S conversion in N₂ are H₂ and S.

For H₂S in H₂, the major product of electron collision with H₂ is atomic H because the dissociation energy of H₂ (4.4 eV) is far less than the excitation energy of the first excited state of H₂ (11 eV),⁴⁷ which results in all excited states of H₂ preferentially dissociating to H radicals:

Atomic H further contributes to H₂S conversion and formation in an autocatalytic manner through the following sequence of reactions:

At low H_2S concentrations, most electrons collide with the balance gas, which suggests that pathway (IV) through reactions R6 and R7 is the major pathway for H_2S conversion. R8 and R9 are responsible for initiating H_2S conversion in Ar, R11 and R12 are responsible for initiating H_2S conversion in He, R15 and R19 are responsible for initiating H_2S conversion in N_2 , and R20 and R21 are responsible for initiating H_2S conversion in H_2 . With increasing H_2S concentration, the H_2S conversion rate through reaction R5 increases. Moreover, the increasing rate of H_2S conversion through R5 is expected to be larger than the decreasing rate of M^* formation through R6 (which further contributes to H_2S dissociation through R7) with increasing H_2S concentration because the dissociation energy of H_2S (3.4 eV) is far less than the excitation energy of Ar (11.55 eV for $\text{Ar}(^3\text{P}_2)$), He (19.82 eV for $\text{He}(2^3\text{S}_1)$), N_2 (6.1 eV for $\text{N}_2(\text{A})$), and the dissociation energy of H_2 (4.4 eV). This explains an initial increase in H_2S conversion rate with increasing H_2S concentration, as shown in Figure 6. However, H_2S is electronegative.²⁰ The presence of an electronegative gas as a reactant reduces the discharge current by capturing electrons and thus reduces the electron concentration during discharge as a result of the electron affinity of H_2S , which results in a decreasing rate of electron collision reactions, as observed previously.^{28, 51, 52} With increasing H_2S concentration, the electronegative effect of H_2S becomes more and more prominent, which finally results in the decreasing rates of electron collision reactions of both R5 and R6. These effects explain the maximum and subsequent decrease of H_2S conversion rates with increasing H_2S concentration, as shown in Figure 6.

Figure 7 shows energy consumption during H_2S conversion as a function of H_2S mole fraction in four balance gases. The energy consumption of H_2S conversion initially decreases,

reaches a minimum, and increases with increasing H_2S mole fraction, which is consistent with the trend of H_2S conversion rate shown in Figure 6. Energy consumption of H_2S conversion in H_2 is higher than that in N_2 . This is because H_2 is smaller than N_2 (as shown by the respective bond lengths of 74 pm versus 110 pm),²¹ which causes a lower rate of electron collision reactions with H_2 compared to N_2 . Energy consumptions of H_2S conversion in Ar and He are the lowest of the tested gases and similar in magnitude. N_2 and H_2 are diatomic molecules while Ar and He are atomic molecules.

Figure 7. Energy consumption of H_2S conversion as a function of H_2S mole fraction in several balance gases: (■): H_2S in Ar, (□): H_2S in He, (▲): H_2S in N_2 , (△): H_2S in H_2 .

Figure 8 is a schematic showing electron collision processes for H_2S in atomic and diatomic balance gases. When an energetic electron collides with an atomic molecule, the electron predominantly experiences elastic collision without energy loss if the electron energy is less than the excitation energy of target atomic molecule. The electron is then further accelerated in the electric field and hence gains more energy. If the electron collides with H_2S in the next collision, H_2S can be dissociated easily because the electron has already experienced two

accelerations over approximately two mean free path lengths of the gas molecules. When an energetic electron collides with a diatomic molecule, the electron can lose energy through many energy levels available to the diatomic molecule, including processes such as dissociation, excitation, rotation and vibration, depending on electron energy. For example, an energetic electron would be deactivated by contributing its energy to rotation and vibration of the diatomic molecule if the electron energy is less than excitation energy or dissociation energy. This implies that electrons cannot gain energy as efficiently in a diatomic balance gas compared to monatomic gases. However, the energy of these electrons in atomic gases can be further utilized because there are no paths for energy loss to rotation and vibration. Therefore, energy efficiency for H_2S conversion in atomic balance gases is expected to be higher than that in diatomic balance gases, which explains the results in Figure 7.

Figure 8. Electron collision processes for H_2S in the atomic and diatomic balance gases.

The results shown in Figure 7 indicate that the lowest energy consumption (highest efficiency) of H_2S conversion is $17 \text{ eV}/\text{H}_2\text{S}$, which is lower than energy consumption reported in other investigations^{4, 5, 12-17} other than H_2S conversion in microwave discharge at low pressure ($\sim 4.5 \text{ eV}/\text{H}_2\text{S}$).² Though the best (lowest) experimental values for energy consumption during

H₂S conversion found during the present investigation are far higher than the dissociation energy of 0.21 eV/H₂S, an improvement of 5 times appears possible through optimizing operating condition and reactor design. If this could be achieved, the dissociation of H₂S into sulfur and useful hydrogen would be an economically attractive plasma process.

Conclusion

A PCD reactor has been fabricated and used to dissociate H₂S into hydrogen and sulfur. A nonthermal plasma cannot be produced in pure H₂S with our reactor geometry (even up to 30 kV discharge voltages) because of the high dielectric strength of pure H₂S (~2.9 times higher than air). Therefore, H₂S was diluted in another gas with a lower breakdown voltage (or dielectric strength). Breakdown voltages of H₂S in four balance gases (Ar, He, N₂ and H₂) have been measured at different H₂S concentrations and pressures. Breakdown voltages are proportional to partial pressure of H₂S and balance gas. H₂S conversion rates and energy efficiencies depend on the balance gas and H₂S inlet concentrations. With increasing H₂S concentrations, H₂S conversion rate initially increases, reaches a maximum, and then decreases. H₂S conversion in atomic balance gases, such as Ar and He, is more efficient than that in diatomic balance gases, such as N₂ and H₂. These observations can be explained by the proposed reaction mechanisms of H₂S dissociation in the different balance gases. The results show that nonthermal plasma technique is effective for dissociating H₂S into hydrogen and sulfur.

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