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Production of Hydrogen and Sulfur from Hydrogen Sulfide in a Nonthermal-Plasma Pulsed Corona Discharge Reactor

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Abstract

Hydrogen sulfide (H_2S) dissociation into hydrogen and sulfur has been studied in a pulsed corona discharge reactor (PCDR). Due to the high dielectric strength of pure H_2S (~2.9 times higher than air), a non-thermal plasma could not be sustained in pure H_2S at discharge voltages up to 30 kV with our reactor geometry. Therefore, H_2S was diluted with another gas with lower dielectric strength to reduce the breakdown voltage. 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. With increasing H_2S concentrations, H_2S conversion initially increases, reaches a maximum, and then decreases. H_2S conversion and the reaction energy efficiency depend on the balance gas and H_2S inlet concentrations. 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 proposed reaction mechanisms 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 source of H_2 . Hydrogen sulfide would have a much higher economic value if both sulfur and chemically pure hydrogen could be recovered instead of merely sulfur. Therefore, processes for direct dissociation of H_2S into H_2 and sulfur are desirable.

Many methods have been investigated to dissociate H_2S into its constituent elements, including thermal decomposition, both noncatalytic and catalytic, electrochemical methods, photochemical methods, and plasma methods (Zaman and Chakma, 1995). Compared to electrochemical and photochemical methods, thermal decomposition and plasma decomposition are promising because of relatively low energy consumption (Cox et al., 1998). However, the thermal decomposition reaction of H_2S is endothermic with low equilibrium conversions even at high temperatures (Kaloidas and Papayannakos, 1987). For example, thermal decomposition of H_2S has an equilibrium conversion of 12% at 1000°C and 1 atmosphere pressure that decreases to less than 1% at temperatures below 550°C . Therefore, two methods have been 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 [Zaman and Chakma (1995) and references therein]. The other is creation of a nonthermal equilibrium environment for H_2S conversion, as found in nonthermal plasmas. Non-thermal plasmas are characterized by

low gas temperature and high electron temperature wherein 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 neutrals, and ions, that can promote chemical reactions at ambient temperatures. Therefore, nonthermal plasmas overcome the disadvantage of the need for high temperatures 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 required to be achieved.

Direct dissociation of H₂S has been investigated using various plasma processing technologies, including arc discharge or thermal plasmas, microwave plasma, glow discharge, silent discharge, and pulsed corona discharge. Dalaine et al. (1998a,b) 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 molecule dissociated. The theoretical minimum energy requirement for the decomposition of H₂S is over three orders of magnitude less than this. For the reaction: $\text{H}_2\text{S}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{S}(\text{s})$, $\Delta H_{298} = 0.21 \text{ eV/H}_2\text{S} = 20.3 \text{ kJ/mol}$. A large amount of work on microwave decomposition of H₂S has been carried out in the former Soviet Union (Asisov et al., 1985; Bagautdinov et al., 1992, 1993a,b, 1995, 1998), where both laboratory and pilot units were reportedly used for the decomposition of pure H₂S or mixtures with CO₂ with a very low energy consumptions of ~0.76 eV/H₂S. Encouraged by these reports of high conversions and low energy requirements, a joint project for H₂S conversion using microwave plasmas was undertaken by The Alberta Hydrogen Research Program, the

Atomic Energy of Canada, and Shell Canada Limited. Unfortunately, this group reported the energy consumption for H_2S conversion to be about 4.5 eV/ H_2S (Cox et al., 1998) and thus was unable to reproduce the low energy consumption reported by the Russian researchers. All microwave plasma experiments for H_2S conversion were performed at pressures below 1 atmosphere, which requires additional energy consumption for compression and vacuum costs. Traus et al. (1992, 1993) investigated conversion of H_2S at 10-100% concentrations in Ar, N_2 , and H_2 in a silent discharge reactor and a rotating glow discharge reactor. They concluded that the energy consumption for H_2S conversion in a rotating glow discharge reactor (~ 27 eV/ H_2S) is less than that in a silent discharge reactor (~ 81 eV/ H_2S). In addition, Abolentsev et al. (1995) and Ma et al. (2001) investigated decomposition of low (ppm) concentrations of H_2S in different balance gases including air, N_2 , H_2 , He, and CH_4 using a silent discharge reactor. H_2S conversion in pulsed corona discharge reactors was also investigated by several investigators (Helfritch, 1993; Ruan et al., 1999; Wiseman and Douglas, 1972; Averin et al., 1996). These investigations were conducted at low H_2S concentrations ($<2\%$) with high (>100 eV/ H_2S) energy consumption, which are not practical conditions for commercial application.

Despite this extensive research on H_2S conversion, many questions remain unanswered. First, all of the research described above has been performed either below atmospheric pressure or at low H_2S concentrations ($<2\%$). H_2S conversion at pressures above atmospheric and at high H_2S concentrations is desirable to determine if nonthermal plasmas have potential for industrial application.

Second, there are no reports on the breakdown voltage of H_2S at pressures higher than atmospheric and H_2S concentrations $>2\%$. Gases at normal temperatures and pressures contain very low concentrations of current carriers (free electrons and ions) and therefore behave as

insulators. In an electric field, any electrons or ions present are accelerated over a distance corresponding to their mean free path between collisions. If they gain enough kinetic energy to ionize gas molecules, they create new current carriers which in turn ionize more molecules. This avalanche-like process forms channels of conducting plasma called streamers. The electrical resistance of the gas between the electrodes becomes nearly zero. This transition of a gas between the insulating and conducting states is known as breakdown. The voltage at which it occurs is called the breakdown voltage. The specific breakdown voltage depends on the gas, as well as on the electrode geometry, the electrode composition, and the gas pressure (Lide, 2003). Breakdown voltage data are important because they define the operating limits for the reaction.

H₂S is an electronegative gas with a high dielectric strength of about 2.9 (Christophorou et al., 1987). Common gases like air, N₂, H₂, He, and Ar have very low dielectric strengths of 1, 1, 0.5, 0.15, 0.18, respectively (Lide, 2003). Therefore, much higher applied 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 during the process of electrical breakdown (Zhao et al., 2005a). As the mean free path of gas molecules increases with decreasing gas pressure, individual electrons gain more kinetic energy in low pressure plasmas than in high pressure plasmas under otherwise similar operating conditions (Zhao et al., 2005a), which causes the breakdown voltage of a gas to decrease with decreasing gas pressure. Therefore, the electrical breakdown of H₂S at either low pressure or low H₂S concentration in a balance gas with a low dielectric strength is comparatively easy, whereas, the 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) (Lide, 2003), Ma et al.(2001) and Helfritsch (1993) proposed that the H₂S conversion mechanism in any of these gases involves ionization of H₂S ($e + H_2S \rightarrow H_2S^+ + 2e$) and subsequent charge neutralization with dissociation ($H_2S^+ + e \rightarrow HS + H$). Abolentsev et al. (1995) proposed an alternate three step mechanism for H₂S conversion: (1) the balance gas (M) is ionized to M⁺, (2) H₂S⁺ is formed by charge transfer reaction ($M^+ + H_2S \rightarrow M + H_2S^+$), and (3) H₂S is dissociated by reaction with an ionized H₂S molecule ($H_2S^+ + H_2S \rightarrow H_3S^+ + HS$). However, neither of these mechanisms may appropriately represent the actual process because the ionization degree in nonthermal plasmas is quite low. A recent investigation by Zhao et al. (2006a) showed that ionization reactions in nonthermal plasmas are negligible. Alternately, Traus et al. (1992, 1993) proposed that radicals, such as H and HS, formed in the plasma are responsible for H₂S conversion.

Therefore, the goals of this work are to investigate breakdown voltage and conversion mechanism of H₂S in four balance gases (Ar, He, N₂, and H₂) in a pulsed corona discharge reactor (PCDR) at higher pressures (above atmospheric) and H₂S concentrations ($\geq 4\%$) than previously reported. A PCDR was chosen to investigate H₂S conversion because (1) PCD plasmas have been extensively investigated and used in methane (Yao et al., 2001) and NO_x conversion (Zhao et al., 2004a,b, 2005b,c) and (2) comparison of energy efficiency of methane conversion among three types 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 (Zhao et al., 2006b).

Experimental Section

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 was 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 capacitors were 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 during 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. A sulfur trap immersed in ice water at the reactor discharge was filled with stainless steel wool to enhance heat transfer and surface area for sulfur vapor removal from the exit gas.

The four gas mixtures of H_2S in Ar, H_2S in He, H_2S in N_2 , and H_2S in H_2 were prepared by mixing ultra high purity (UHP) H_2S with the UHP balance gas. Gas mixtures flowed through PCDR at entrance conditions of ambient temperature ($\sim 300K$) and a controlled pressure. The highest pressure used in this work was 5.0 bar. The desired entrance mole fraction of H_2S was achieved by setting flowrates of H_2S 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 ($J \cdot s^{-1}$), was calculated as the product of the input energy per pulse and the pulse frequency, $\frac{1}{2}fCV_c^2$, where f is the pulse frequency in Hz. The gas leaving the sulfur condenser was analyzed using an online Residual Gas Analyzer (RGA, Stanford Research Systems, Inc. QMS100), which is a quadrupole mass spectrometer. To perform quantitative measurements, an internal standard method (Watson, 1997) was used to calibrate the ion signal response at an m/z ratio of 34 with the H_2S mole fraction, in which the balance gas was used as an internal standard. The calibration results are shown in Figure 2.

Figure 2 shows the ratio of the H_2S and balance gas mole fractions as a function of the measured H_2S and balance gas intensities, which show a 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, N_2 , or H_2 . Therefore, the measured ion current ratio of H_2S and the balance gas can be used to determine the mole fraction ratio, K, of H_2S and the balance gas from Figure 2. For a binary gas mixture at the reactor entrance, the mole fraction of H_2S 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, H_2S dissociates into H_2 and sulfur. For the balance gases Ar, He, and N_2 , the effluent gas mixture is the ternary

system including H₂ because sulfur is captured by the sulfur condenser. However, the mole fraction of balance gas at the reactor outlet is the same as that at the reactor inlet because 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. Conversions based on either H₂S consumption or H₂ production were similar, but the H₂S data provided higher accuracy. Mass balances could not be accurately calculated because not all sulfur was trapped in the condenser and some deposited on the reactor wall and the reactor outlet tube that could not be recovered for weighing. However,

the amount of sulfur recovered was consistent with the reported conversions. Energy Dispersive Spectroscopy and X-ray diffraction were used to analyze the sulfur product.

Results and Discussion

Breakdown voltage of H₂S in the various balance gases. Gas breakdown voltage depends on the specific reactor configuration, especially the electrode configuration and structure. Breakdown voltages of many pure gases have been investigated in both uniform and non-uniform fields.(Blair, 1978) For uniform fields, the breakdown voltage usually follows Paschen's law, which states that breakdown voltage, V_b , is a function of nd only, where n is the gas number density ($\text{molecules}\cdot\text{cm}^{-3}$) 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 (Blair, 1978). For the PCDR used in this work, r is the radius of wire anode. For many pure gases in non-uniform fields, the breakdown voltage is proportional to nr at pressures higher than 0.5 bar (Blair, 1978).

Gas breakdown can be detected by the discharge waveform recorder, shown in Figure 1. In addition, the audible discharge noise from PCDR can also be clearly heard when the corona discharge occurs. The breakdown voltage was determined by increasing the charge voltage in increments of 0.1 kV from a low value at which no discharge occurs until the discharge is detected by both the discharge waveform recorder and the audible noise from the reactor. The measured breakdown voltages at different pressures for pure Ar, H₂, and N₂ are shown in Figure 3. For this reactor, the anode radius, r , is 0.0005 m and the inlet temperature is 300 K. At these conditions, 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 (Blair, 1978). Breakdown voltages of pure N₂ measured at flowrates of 1.18×10^{-4} SCM·s⁻¹ and 7.87×10^{-6} SCM·s⁻¹ are almost the same, which indicates no effect of gas flowrate on breakdown voltage. In addition, pulse frequencies above 300 Hz do not affect breakdown voltage.

Breakdown of pure He occurred at any pressure from 0.8 to 5.0 bar at the lowest charge voltage of 6.9 kV used in this work. However, breakdown of pure H₂S did not occur over the entire operation range for our reactor, which included pressures from 0.8 to 5.0 bar and charge voltages from 6.9 to 30 kV. These results combined with the results in Figure 3 indicate that the order of increasing breakdown voltage at constant pressure is: He < Ar < H₂ < N₂ < H₂S, which is consistent with the order of increasing dielectric strength of these gases (dielectric strength of He: 0.15, Ar: 0.18, H₂: 0.50, N₂: 1.0, H₂S: 2.9) (Christophorou et al., 1987; Lide, 2003).

Because no corona was formed in pure H₂S at the maximum charge voltage (30 kV) with this reactor geometry, H₂S was mixed with another gas with lower dielectric strength to initiate electrical discharge. He, Ar, N₂, and H₂ were used as balance gases in this work because they do not produce byproducts in the corona.

As neither gas flowrate nor pulse frequency (>300 Hz) affect breakdown voltage, gas breakdown experiments were performed 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), according to

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

where P_t is the total gas pressure in bar and m_i and n_i are the slope and the intercept at a specific H_2S mole fraction, respectively. Figure 4(b) shows the slope m_i and the intercept n_i as a function of H_2S mole fraction. These results show that the slope m_i is proportional to H_2S 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 for the linear relationship of m_i and H_2S mole fraction, respectively, and P_{H_2S} and P_{H_2} are the partial pressures of H_2S and H_2 , 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 the partial pressures of the components in binary gas mixtures. Parameters a_2 , b_2 , and c were obtained through a least-square regression analysis by application of Equation (11) to mixtures of H_2S in Ar, H_2S in He, H_2S in N_2 , and H_2S in H_2 . The breakdown voltages (V_b) are,

$$H_2S \text{ in Ar: } V_b \text{ (kV)} = 22.2 \times P_{H_2S} \text{ (bar)} + 2.52 \times P_{Ar} \text{ (bar)} + 6.48 \quad (12a)$$

$$H_2S \text{ in He: } V_b \text{ (kV)} = 16.2 \times P_{H_2S} \text{ (bar)} + 2.42 \times P_{He} \text{ (bar)} + 3.35 \quad (12b)$$

$$H_2S \text{ in } N_2: V_b \text{ (kV)} = 16.1 \times P_{H_2S} \text{ (bar)} + 6.44 \times P_{N_2} \text{ (bar)} + 4.00 \quad (12c)$$

$$H_2S \text{ in } H_2: V_b \text{ (kV)} = 15.2 \times P_{H_2S} \text{ (bar)} + 4.74 \times P_{H_2} \text{ (bar)} + 2.70 \quad (12d)$$

These correlations are valid for total absolute pressures between 0.8 bar and 3.6 bar and geometrically similar coaxial cylinder reactor systems. Figure 5 shows the experimental results and the fitted data using Equations 12(a)-(d). Most experimental data matched the fitted data, except for low concentrations (<4%) of H_2S in Ar. In this exceptional case, an increase in gas pressure causes the breakdown voltage to deviate from linearity at intermediate pressures before

returning to linearity with a similar slope with a new intercept. Similar experimental results are obtained for 2% H₂S in Ar, but the reason for this exception is not yet clear.

H₂S conversion in various balance gases. Experiments on H₂S conversion in Ar, He, N₂, and H₂ were carried out at a fixed pulse 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 1.18×10^{-4} SCM·s⁻¹, corresponding to a 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 mixtures of H₂S in Ar, H₂S in He, H₂S in N₂, and H₂S in H₂ at the total pressure of 1.34 bar, which confirmed that electrical discharges occur. Sulfur deposits in the sulfur condenser, as well as the reactor tube and outlet, further confirmed the active discharge. The presence of sulfur was confirmed by Energy Dispersive Spectroscopy. The first two principal peaks for orthorhombic α -sulfur were observed in the X-ray diffraction data.

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

There are four proposed mechanisms for H₂S conversion in nonthermal plasmas.

(I) Direct ionization of H₂S followed by dissociative neutralization (Ma et al., 2001; Helfrich, 1993):

(II) Ionization of the balance gas (M), leading to charge transfer reaction, and subsequent dissociative recombination (Abolentsev et al., 1995):

(III) Direct electron collision dissociation of H₂S:

(IV) Electron collision dissociation or excitation of the balance gas, which produces active species that 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, an increasing number of H₂S molecules should be ionized with increasing H₂S concentration, which should lead to increasing H₂S conversion rate 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 must 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 (Zhao et al., 2006a), 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 (van Veldhuizen et al., 1996). In the streamer head, the concentration of ions (corresponding to the concentration of electrons) is around 15 ppm (Zhao et al., 2006a). If pathways (I) and (II) are responsible for H_2S conversion and all cations formed from reactions R1 and R3 contribute to H_2S conversion, the conversion of H_2S for initial H_2S mole fractions of 0.04 is $400 \text{ Hz} \times 4.25 \text{ s} \times 15 \text{ ppm} \times (10^{-4} - 10^{-3}) / 0.04 = 0.064$ - 0.0064% , which is at least two orders of magnitude lower than the H_2S conversions observed during the experiments, as shown in Figure 6. Therefore, the observed H_2S conversion solely through ionic reactions is not possible.

Conversion of H_2S through pathways (III) and (IV) can be supported by the following points:

(1) As demonstrated by Eliasson and Kogelschatz (1986, 1991), the concentration of radicals and excited states formed from electron collision reactions in the streamer head is 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 (Zhao et al., 2006a). Therefore, if reactions R5-R7 contribute to H_2S conversion, the conversion of H_2S for initial mole fractions of 0.04 is $400 \text{ Hz} \times 4.25 \text{ s} \times (10^4 \times 15 \text{ ppm}) \times (10^{-4} - 10^{-3}) / 0.04 = \sim 64\%$, which exceeds all the experimental results shown in Figure 6. However, this result is reasonable because the efficiency of such plasma reactions is less than 100%.

(2) The occurrence of H_2S conversion through direct electron collision reaction R5 is suggested by the experimental data on H_2S conversion in He. Our previous study of Ar plasma

in PCDR's (Zhao et al., 2006c) showed that the main active species formed during electron collision reactions with Ar are excited states and not cations. By analogy, the main active species contributing to H₂S conversion formed from electron collision reaction with He are assumed to be excited states of He and the contribution of ions to H₂S conversion in He is excluded from consideration. The first electronic excited state of He, He(2³S₁), has an excitation energy of 19.82 eV (Prestage et al., 1985). 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 would be 110 W/(19.82 eV × 96.5 kJ/eV mol) = 57.5 μmol/s. However, for concentrations of H₂S in He less than 12%, the conversion rates of H₂S are all higher than 57.5 μmol/s, which indicates that direct electron collision reaction of H₂S (R5) must 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 investigation (Zhao et al., 2006c) 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 (Velazco et al., 1978; Gundel et al., 1976):

Similarly, the following reactions contribute to H₂S conversion for H₂S in He (Bevsek et al., 1995; Someda et al., 1988; Yenchu and Wu, 1978):

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

For H_2S in N_2 , the major products of electron collision reactions with N_2 are N radicals and $\text{N}_2(\text{A})$, the first electronic excited state of N_2 (Zhao et al., 2004c).

Previous investigation (Zhao et al., 2005a) has shown that the rate of electron collision reaction R15 is about 7 times higher than that of R14. These active species react with N_2 , H_2S , and H_2 (Herron, 1999; Aleksandrov et al., 1994; Kossyi et al., 1992), as follows:

There are no reports of reaction of H_2S and N. However, by analogy with the extremely low rate constant for the reaction of N with H_2O ($4 \times 10^3 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ at 1073 K) (Cohen and Westberg, 1991), we presume that N does not contribute significantly to H_2S conversion and that N radicals predominantly recombine to form N_2 because the rate constant for this recombination reaction (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 H_2S conversion in N_2 are H_2 and S.

For H_2S in H_2 , the major product of electron collision with H_2 is atomic H because the dissociation energy of H_2 (4.4 eV) is far less than the excitation energy of the first excited state

of H₂ (11 eV) (Sharp, 1971), which results in all electronic 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 (Peng et al., 1999; Stachnik and Molina, 1987; Schofield, 1973):

At low H₂S concentrations, most electrons collide with the balance gas, which suggests that pathway (IV) through reactions R6 and R7 is the major pathway for H₂S conversion. R8 and R9 are responsible for initiating H₂S conversion in Ar, R11 and R12 are responsible for initiating H₂S conversion in He, R15 and R19 are responsible for initiating H₂S conversion in N₂, and R20 and R21 are responsible for initiating H₂S conversion in H₂. With increasing H₂S concentration, the H₂S conversion rate increases because the rate of direct electron collision dissociation of H₂S (R5) increases. Moreover, the increasing rate of H₂S conversion through R5 is expected to be larger than the decreasing rate of M* formation through R6 (which further contributes to H₂S dissociation through R7) with increasing H₂S concentration because the dissociation energy of H₂S (3.4 eV) is far less than the excitation energy of Ar (11.55 eV for Ar(³P₂)), He (19.82 eV for He(2³S₁)), or N₂ (6.1 eV for N₂(A)), and the dissociation energy of H₂ (4.4 eV). This explains the initial increase in H₂S conversion rate with increasing H₂S concentration, as shown in Figure 6. However, H₂S is electronegative (Christophorou et al., 1987). The presence of an electronegative gas as a reactant reduces the discharge current in the reactor by capturing

electrons. Thus, the electron concentration during discharge is reduced due to the high electron affinity of H_2S , which results in a decreasing rate of electron collision reactions, as observed previously (Zhao et al., 2005d,e). With increasing H_2S concentration, the electronegative effect of H_2S becomes more prominent and finally results in decreasing rates of electron collision reactions (R5 and R6). These effects explain the maxima and subsequent decrease of H_2S conversion rates with increasing H_2S concentration shown in Figure 6.

Figure 7 shows energy consumption during H_2S conversion as a function of H_2S mole fraction in the 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 during H_2S conversion in H_2 is higher than in N_2 because the cross sectional area of molecular H_2 is 1.86 times smaller than that of N_2 (as shown by the respective effective molecular radius of 1.35 versus 1.84 Å) (Daubert and Danner, 1997), which causes a lower rate of electron collision reactions with H_2 compared to N_2 and results in more energy dissipation in H_2 compared to N_2 . Energy consumption during H_2S conversion in Ar and He are the lowest of the tested gases and similar in magnitude.

Energy consumption during H_2S conversion in monatomic balance gases is far lower than in diatomic balance gas, which can be explained through analysis of electron collision processes for H_2S in the monatomic 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 atom. 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 the many energy levels available to diatomic molecules, including excitation, rotation, vibration, and dissociation, depending on the 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. The electron energy in atomic gases can be used more efficiently because there are no paths for energy loss to rotation and vibration. Therefore, energy efficiency of H₂S conversion in atomic balance gases is expected to be higher than that in diatomic balance gases, as observed in Figure 7.

The results in Figure 7 show that the lowest energy consumption (highest efficiency) of H₂S conversion is 17 eV/H₂S. This value is lower than the energy consumption reported in all previous investigations (Helfrich, 1993; Ruan et al., 1999; Abolentsev et al., 1995; Ma et al., 2001; Traus and Suhr, 1992; Traus et al., 1993; Dalaine et al., 1998a,b), except in microwave discharges at sub-atmospheric pressures (~4.5 eV/H₂S) (Cox et al., 1998). This result confirms that pulsed corona discharges are more efficient than other types and that relatively low energy consumption can be obtained at high pressures and H₂S concentrations. However, most hydrogen produced industrially by steam reforming of methane and other light alkanes has an energy consumption of 3.92 eV/H₂ (Cox et al., 1998), which is a factor of 4 less than the best (lowest) experimental values for energy consumption during H₂S conversion found during the present investigation. Thus, further improvements in plasma efficiency must be achieved before plasma processes can compete with current hydrogen production methods.

Conclusions

Breakdown voltages of H_2S in four balance gases (Ar , He , N_2 and H_2) measured at different H_2S concentrations and pressures are proportional to the partial pressures of H_2S and the respective balance gas. H_2S conversion rates and energy efficiencies depend on the balance gas and H_2S inlet concentrations. With increasing H_2S concentrations, H_2S conversion rates initially increase, reach a maximum, and then decrease. 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 reaction mechanisms that involve electron collision reactions either with H_2S that cause direct dissociation or with the balance gas to produce active species in electronic excited states that then relax by dissociating H_2S . The results show that nonthermal plasmas are effective for dissociating H_2S into hydrogen and sulfur, but further increases in energy efficiency are necessary.

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Figure Captions

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.

Figure 2. Calibration plot for H₂S relative to the balance gas used as an internal standard.

Figure 3. Breakdown voltage of pure gases as a function of pressure.

(■): Ar at 1.18×10^{-4} SCM·s⁻¹ and 400 Hz; (●): H₂ at 1.18×10^{-4} SCM·s⁻¹ and 400 Hz; (▲): N₂ at 1.18×10^{-4} SCM·s⁻¹ and 400 Hz; (▼): N₂ at 7.87×10^{-6} SCM·s⁻¹ and 400 Hz

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 from linear regression in (a) as a function of H₂S mole fraction. (■): slope m_i ; (▲): intercept n_i .

Figure 5. Breakdown voltage as a function of total gas pressure. (a) H₂S in Ar; (b) H₂S in He; (c) H₂S in N₂; (d) H₂S in H₂

Experimental data: (□): 4% H₂S; (○): 8% H₂S; (△): 12% H₂S; (▽): 16% H₂S; (◇): 20% H₂S; (+): 25% H₂S; (×): 30% H₂S
Calculated data: (—): 4% H₂S; (— —): 8% H₂S; (···): 12% H₂S; (- · -): 16% H₂S; (- · · -): 20% H₂S; (---): 25% H₂S; (- · - ·): 30% H₂S

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

Figure 7. Energy consumption of H₂S conversion as a function of H₂S mole fraction in different balance gases. (■): H₂S in Ar, (□): H₂S in He, (▲): H₂S in N₂, (△): H₂S in H₂

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 (▲): N_2 at $1.18 \times 10^{-4} \text{ SCM}\cdot\text{s}^{-1}$ and 400 Hz; (▼): N_2 at $7.87 \times 10^{-6} \text{ SCM}\cdot\text{s}^{-1}$ and 400 Hz

Figure 4. Breakdown voltage of H_2S in H_2 . (a) Breakdown voltage as a function of total gas pressure. Experimental data: (□): 4% H_2S , (○): 8% H_2S , (△): 12% H_2S , (▽): 16% H_2S , (+): 25% H_2S ; linear regression: (—): 4% H_2S , (---): 8% H_2S , (···): 12% H_2S , (— · —): 16% H_2S , (---): 25% H_2S . (b) Slope and intercept from linear regression in (a) as a function of H_2S mole fraction. (■): slope m_i ; (▲): intercept n_i .

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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 ; (- · -): 16% H_2S ;
(- · · -): 20% H_2S ; (---): 25% H_2S ; (- · -): 30% H_2S

Figure 6. H₂S conversion and conversion rate as a function of H₂S mole fraction in different balance gases. ($\square$): conversion, ($\blacksquare$): conversion rate

Figure 7. Energy consumption of H₂S conversion as a function of H₂S mole fraction in different balance gases. (■): H₂S in Ar, (□): H₂S in He, (▲): H₂S in N₂, (△): H₂S in H₂