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ABSTRACT

This paper presents the results of experiments in which various parameters were varied systematically in an attempt to understand how the reactor design affects the energy efficiency for plasma processing of NO_x. These parameters include the packing material, electrode diameter, and voltage frequency. It is shown that the applied voltage is not the relevant parameter when comparing the performance of different plasma reactors. The important control parameter is the input energy density. In accordance with the observations reported by Penetrante *et al.* [*Applied Physics Letters* 68, 3719-3721 (1996)], we have found that reactor design has little influence on the basic energy consumption of the plasma. Consequently, different reactor designs should yield basically the same plasma chemistry if the experiments are performed under identical gas composition and temperature conditions.

INTRODUCTION

A critical issue in the use of plasmas for the treatment of NO_x is the electrical energy consumption. Whether the plasma is used to directly reduce NO_x in the gas phase, or utilized to produce partial oxidation intermediates that enhance the heterogeneous removal of NO_x, the electrical energy consumption of the process is a concern. Many ideas have been proposed in attempts to minimize the electrical energy consumption, including (a) optimization of the electrode structure of the plasma reactor, and (b) optimization of the voltage waveform applied to the plasma reactor. It has been difficult to assess and compare the performance of various kinds of plasma reactors. The data presented in the literature using different kinds of reactors often were measured under different gas conditions. In many cases, the data are presented in a way that makes it impossible for the reader to determine the energy consumption of the reactor.

This paper will present the results of experiments in which various parameters were varied systematically in an attempt to understand how the reactor design affects the energy efficiency for plasma processing of NO_x. These parameters include the packing material, electrode diameter, and voltage frequency.

Many papers in the plasma processing literature present their NO_x conversion efficiency as a function of the voltage applied to the plasma reactor. We will show that the applied voltage is not the relevant parameter when comparing the performance of different plasma reactors. Comparisons based on the applied voltage lead to erroneous conclusions. The important control parameter is the energy density delivered to the plasma. We will further show that reactor design has little influence on the basic energy consumption of the plasma. Consequently, different reactor designs should yield basically the same plasma chemistry if the experiments are performed under identical gas composition and temperature conditions.

EXPERIMENTAL CONDITIONS

When dealing with complicated gas mixtures encountered in real exhaust gases, it is often difficult to separate the plasma physics issues affecting electrical energy consumption in the plasma reactor from the plasma chemistry issues affecting the NO_x conversion chemistry. In comparing the effects of electrical and reactor parameters, it is important to carry out simplified experiments in which the number of chemical components is limited. A gas mixture consisting of dilute concentration of NO in N_2 provides a good system for studying the effect of reactor parameters on the electron kinetics in the plasma. In this mixture the overall NO removal mechanism is determined by only a few reactions and the simplicity of the gas mixture allows a precise analysis of the process products. The oxygen balance in the system can be established to confirm that all the products of the plasma processing are accounted for. The analysis of the basic electrical energy consumption is also greatly simplified because the input energy is consumed only in electron-impact reactions with N_2.

All of the experimental results discussed here were obtained using a mixture of dilute concentration of NO in N_2. In this gas mixture the destruction of NO results

mainly in the formation of N_2 and O_2, with only small amounts of NO_2 and N_2O. The NO_x conversion for the NO-N_2 system can therefore be taken as the percentage of NO_x reduction to N_2.

The plasma reactor used in the experiments reported here is a dielectric-barrier discharge reactor. The reactor geometry was one of concentric cylinders. The center and outer cylinders were a solid stainless steel rod and stainless steel tube. A high voltage AC power was applied between the electrodes, with the outer electrode tube at ground potential. Various diameter center electrodes were used, ranging from 0.1 mm to 4 mm. The inner diameter of the outer electrode tube ranged from 22 mm to 25 mm. Dielectric barriers made of quartz were placed adjacent to the center and outer electrodes. One was used to cover the inner electrode and the other was used to cover the inside of the outer electrode. The length of the plasma reactor tube was 30.5 cm. The discharge plasma region could be made shorter than the tube by limiting the length of the center electrode inside the center dielectric barrier, which ran the full length of the reactor and provided mechanical support for the electrode. A sketch of the plasma reactor is shown in Figure 1.

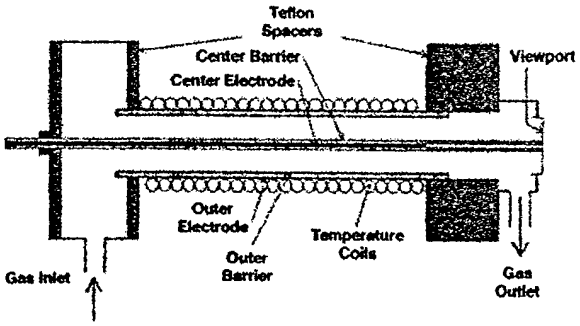

Figure 1. Sketch of the dielectric-barrier discharge reactor used in this study.

High voltage AC power was supplied to the plasma reactor. A variable voltage (0-120 V), variable frequency (20-20,000 Hz) power supply was used to power a high voltage transformer. The transformer was rated at a primary voltage of 120 V, a secondary voltage of 25 kV and a power limit of 0.5 KVA. The power supply and the power measurement is discussed in detail in an accompanying paper [1].

To characterize the electrical energy consumption of the process, the composition of the effluent gas was recorded as a function of the input energy density. The input energy density, in units of Joules per standard liter (J/L), is the ratio of the power (deposited into the gas) to gas flow rate at standard conditions (25°C and 1 atm).

The composition of the effluent gas was also recorded as a function of other parameters such as applied voltage, voltage frequency and gas flow rate. There are authors who show comparisons of plasma reactor performance in terms of the applied voltage. We will present our data also in this manner in order to point out that comparisons based on the applied voltage lead to erroneous conclusions. The important control parameter that should be used for comparing plasma reactor performance is the input energy density.

A chemiluminescent NO_x analyzer was used to measure the concentration of oxides of nitrogen in the gas stream entering or exiting from the reactor. The difference between NO and NO_x readings was taken to be NO_2.

N_2O, a possible product in plasma processing of NO, could not be detected by the NO_x analyzer. A Hewlett-Packard 5890 Series II gas chromatograph with a thermal conductivity detector was used to determine if N_2O was present in the reactor exit gas. A 9' by 1/8" stainless steel column packed with 50/80 mesh Porapak T was used to separate N_2O from the other gases in the stream.

CHEMICAL KINETICS

For dilute concentrations of NO in N_2, the input energy required for NO reduction [2-4]:

$$N + NO \rightarrow N_2 + O \qquad \text{(Eq. 1)}$$

is determined by the energy required for dissociation of N_2 [5]:

$$e + N_2 \rightarrow e + N + N. \qquad \text{(Eq. 2)}$$

The input electrical energy is consumed in electron-impact reactions with N_2 and the removal of NO proceeds mainly via reduction by the N atom [6]. By doing experiments using this mixture it is therefore possible to examine the dependence of the dissociation rate of N_2 on the plasma reactor configuration. The dissociation rate of N_2 provides a good measure of the electron mean energy in the plasma. In turn, the electron mean energy provides a measure of the effective E/n that is established in the plasma. E/n is the electric field strength divided by the total gas density.

The calculated G-value (number of N_2 dissociations per 100 eV of input energy) and electron mean energy as a function of E/n is shown in Figure 2. In the NO-N_2 mixture, the number of N_2 dissociations in the plasma can be easily related to the number of NO molecules reduced from the gas. Thus, by measuring the amount of NO reduction, we can get a measure of the electron mean energy in the plasma. We will see that the experimental results presented in this paper all correspond to an electron mean energy between 3.0 and 3.5 eV.

A chemical kinetics analysis of the important reactions during plasma processing of 250 ppm NO in N_2 is shown in Figure 3. Details of the model are discussed by Penetrante et al. [2-3]. The dominant reaction in this mixture is the reduction of NO to N_2 via reaction (1). The O atom resulting from reaction (1) oxidizes NO to NO_2:

$$O + NO + M \rightarrow NO_2 + M \qquad \text{(Eq. 3)}$$

The NO_2 is reduced back to NO:

$$O + NO_2 \rightarrow NO + O_2 \qquad \text{(Eq. 4)}$$

thus resulting in a small amount of NO_2 product. The reduction of NO_x by the N atom is limited by the electron-impact dissociation of N_2.

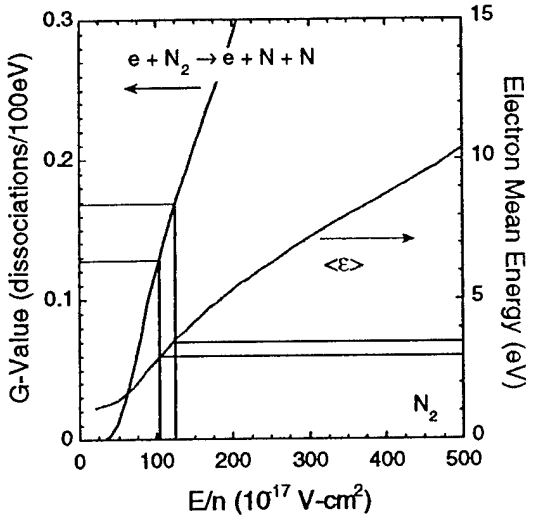

Figure 2. Calculated N_2 dissociation G-value and electron mean energy as a function of effective E/n in the plasma.

Figure 3 shows that the removal of NO is dominated by the reduction reaction $N + NO \rightarrow N_2 + O$; thus, the energy cost for reduction of NO is simply the energy cost for production of N. The only two other important reactions are the oxidation of NO to NO_2 via $O + NO + M \rightarrow NO_2 + M$, and the reduction of NO_2 to NO via $O + NO_2 \rightarrow NO + O_2$. These two latter reactions serve to produce O_2 as the only other major product in addition to N_2. Most of the NO which are oxidized to NO_2 are reduced back to NO; note that this happens only in the NO-N_2 mixture.

In Figure 3, NO is depleted at around 300 J/L. After the initial NO has been depleted, the concentration of N builds up until radical-radical reactions become important. Some of the N then recombine via $N + N + M \rightarrow N_2 + M$; some of the N react with O to produce NO via $N + O + M \rightarrow NO + M$. Any NO produced by the latter process are reduced by other N atoms.

There is very little N_2O produced during the plasma processing of dilute mixtures of NO in N_2. The most likely source of N_2O is the reaction

$$N + NO_2 \rightarrow N_2O + O \qquad \text{(Eq. 5)}$$

In the NO-N_2 mixture, there is little N_2O produced for three reasons. First, the amount of NO_2 formed is small. Second, the N atoms react preferentially with NO, because the rate constant for N + NO is larger, and the amount of NO_2 is always small. Third, the NO_2 produced in this system react preferentially with O (via reaction 4) instead of N, and thus gets reduced to NO instead of N_2O.

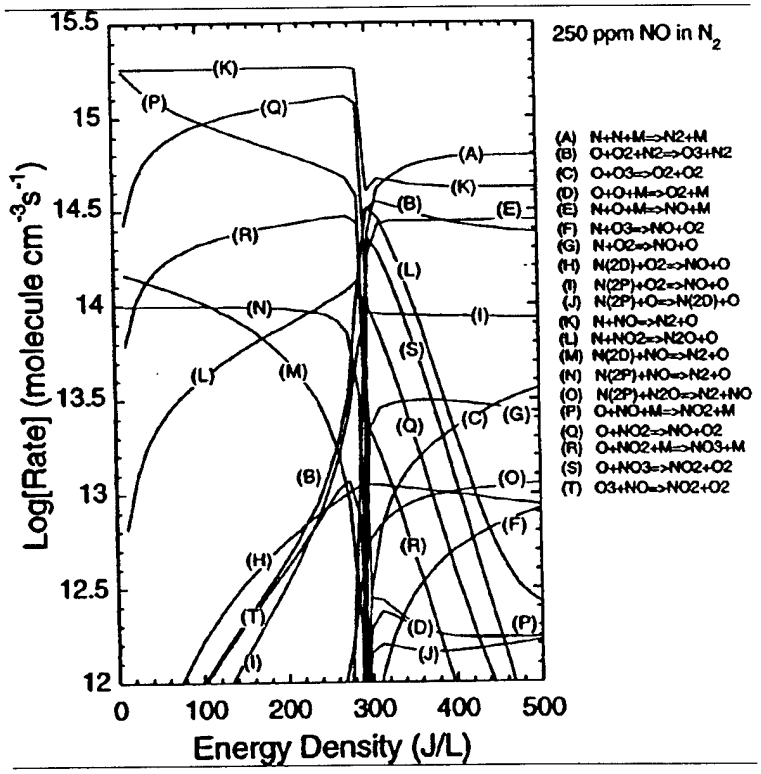

Figure 3. Chemical kinetics analysis of the important reactions during plasma processing of 250 ppm NO in N_2.

EFFECT OF PACKING

The presence of solid materials in the gas space between the discharge electrodes alters the operation of the discharge plasma. Changes in the physical characteristics of the discharge can presumably cause variations in chemical reactions to occur.

A highly conductive material eliminates the discharge through the bulk of the gas region by eliminating the potential difference across the gas. Dielectric materials, on the other hand, provide a greater induced surface charge in the gas space for a given electrode geometry and applied voltage. Additionally, dielectric materials may provide numerous points for the microdischarges to occur, depending on the shape of the material. A high field intensity around the tip of a fiber with a high induced surface charge can produce a microdischarge more easily.

Experiments using several non-conducting materials were performed in this study to investigate their effect in conjunction with a barrier discharge plasma on the NO_x conversion efficiency. The materials included cylindrical molecular sieves as well as glass wool and Kaowool in fiber form. The glass wool and Kaowool used were composed primarily of silica, while the molecular sieves were composed of aluminosilicates.

When the NO_x reduction efficiency is plotted in terms of applied voltage, it appeared as if the NO_x reduction achieved using glass wool and Kaowool in fiber form were higher than that obtained using cylindrical molecular sieves. Additionally, the use of any of the three packing materials resulted in higher NO_x reduction than when no packing was used.

The effect of glass wool packing on NO_x reduction was further investigated in a reactor at room temperature with an inlet gas mixture of 250 ppm NO in N_2. Glass wool packings with densities of 0.12 g/cm^3 and 0.30 g/cm^3, as well as a system with no packing, were used. The results showing NO_x reduction versus applied voltage for the three sets of experiments are shown in Figure 4. It appears as if the systems with glass wool packing resulted in higher NO_x reduction than that without packing.

Packing the reactor gas space results in a change in the electrical power input to the discharge plasma. The applied voltage is not a good parameter with which to compare the performance of different reactors. The input energy density (power input to the gas divided by the total gas flow rate) represents a more relevant physical scaling parameter. The results showing NO_x reduction versus input energy density for the same three sets of experiments are shown in Figure 5. Note that in terms of energy density input to the reactor, there was no significant difference in NO_x reduction achieved in systems with no packing and those with glass wool packing. An increase in the density of the glass wool packing, and therefore an increase in glass wool surface area in the reactor, did not increase the NO_x reduction for a given energy density input to the plasma.

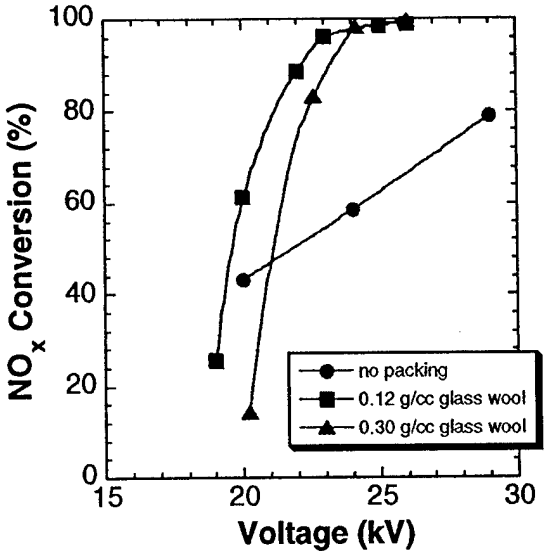

Figure 4. Effect of reactor packing on plasma processing of 250 ppm NO in N_2.

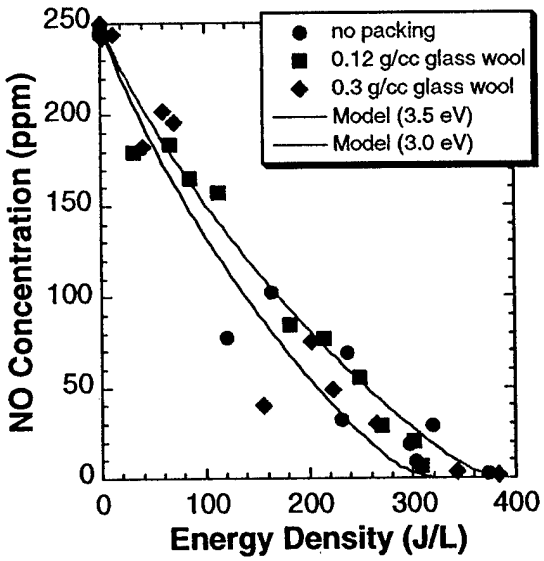

Figure 5. Effect of reactor packing on plasma processing of 250 ppm NO in N_2.

Packing the reactor gas space with dielectric materials increased the capacitance of the reactor, which produced a greater charge concentration on the surface of the reactor electrodes for a given voltage. This was seen in the higher current measured for the packed reactor systems, prior to the onset of the discharge, than that measured without packing material in the reactor. The packed

reactor's higher charge build-up also resulted in a higher discharge current and therefore higher power input to the reactor. It was this increase in power input to the reactor that was responsible for the higher levels of NO_x reduction achieved (versus applied voltage) when the glass wool and Kaowool packings were used.

EFFECT OF ELECTRODE DIAMETER

Visual observations of the discharge plasma showed that the region of greatest discharge intensity occurred around the center electrode, where an intense blue glow was seen in the NO-N_2 system. At the outer electrode the visible glow was faint if it could be seen at all. This was due to the reduced current flux at the outer electrode brought about by the coaxial cylinder geometry. It was recognized that most of the gas in the reactor was outside the intense discharge region. Experiments with outer electrodes of reduced diameter were therefore conducted in an attempt to increase the percentage of the gas in the intense discharge region.

The effect on NO_x reduction of reducing the distance between electrodes by decreasing the outer electrode diameter from 25 mm to 22 mm was studied. A center electrode with a diameter of 4 mm, surrounded by a quartz dielectric barrier (4 mm ID by 6 mm OD) was used in each set of experiments. A second, outer quartz dielectric barrier, with a wall thickness of 1.5 mm, was placed adjacent to the outer electrode in each configuration. The resulting annulus had an inner annulus diameter of 6 mm for both configurations, an outer annulus diameter of 22 mm for the 25 mm outer electrode, and an outer annulus diameter of 18 mm for the 22 mm outer electrode. The experiments were done at room temperature with an inlet gas mixture of 250 ppm NO in N_2.

The results showing NO_x reduction versus applied voltage for the two sets of experiments are shown in Figure 6.

It appears as if the decrease in the electrode gap distance increased the NO_x reduction. However, when the results are plotted in terms of the input energy density, it is clear that decreasing the diameter of the outer electrode or decreasing the electrode gap distance did not increase the NO_x reduction, as shown in Figure 7. The effect of reducing the gap spacing between the electrodes was to increase the power input to the reactor for a given voltage. Since the same center electrode system was used in both sets of experiments, the voltage at which the discharge initiated did not change.

However, because of the reduced distance between the electrodes, the resistance of the gas was decreased and the induced surface charge for a given voltage increased (the capacitance increased) over that for the larger gap space. This resulted in a higher discharge current and greater discharge power for the smaller gap between electrodes.

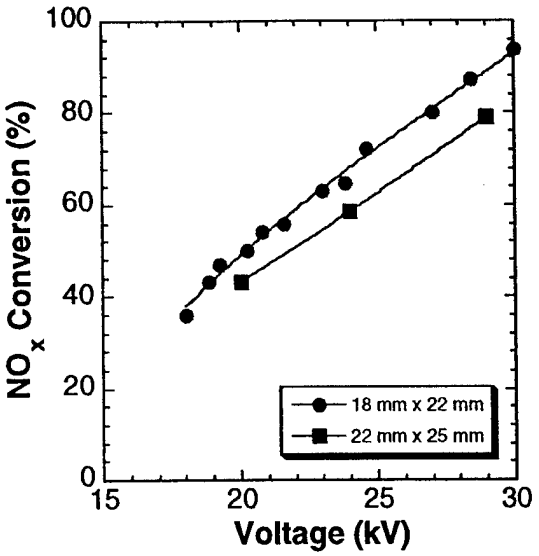

Figure 6. Effect of electrode diameter on plasma processing of 250 ppm NO in N_2.

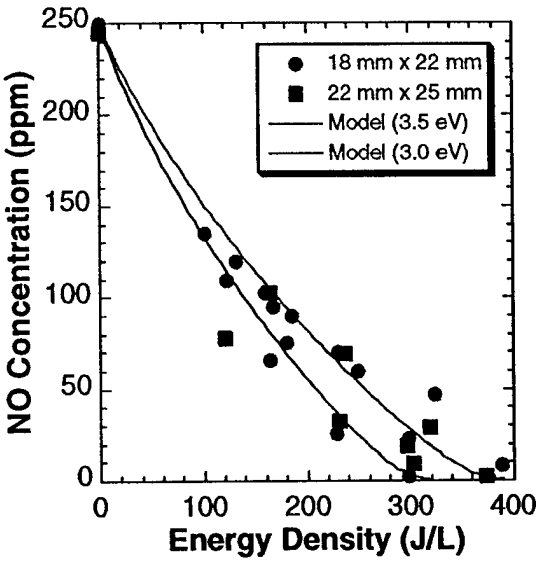

Figure 7. Effect of electrode diameter on plasma processing of 250 ppm NO in N_2.

EFFECT OF FREQUENCY

The effect of frequency on NO_x reduction was studied. The experiments were conducted using a glass wool packing of density 0.12 g/cm^3, and a gas mixture of 250 ppm NO in N_2 at room temperature.

The results showing NO_x reduction versus applied voltage at various frequencies are shown in Figure 8. The NO_x reduction increased with frequency for a given voltage as the frequency was raised. The rate of increase in NO_x reduction versus voltage also increased as the frequency was increased.

When the results are plotted in terms of input energy density, it becomes clear that frequency does not affect the electrical power consumption to achieve a given level of NO_x reduction, as shown in Figure 9. The effect of increasing frequency was to increase the power input for a given peak voltage, or to reduce the voltage required to achieve a given discharge power.

SUMMARY OF DATA

The experimental results shown in the previous sections suggest that the electron mean energy in the plasma reactor is very weakly dependent on reactor parameters such as material packing, electrode gap spacing, and applied voltage frequency. A summary of all the data taken using a gas mixture of 250 ppm NO in N_2 is shown in Figure 10.

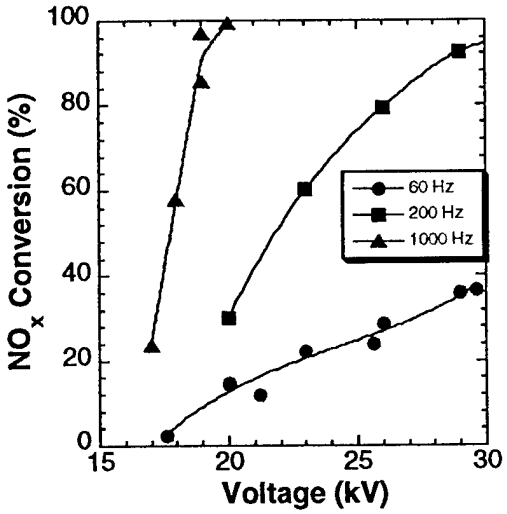

Figure 8. Effect of applied voltage frequency on plasma processing of 250 ppm NO in N_2.

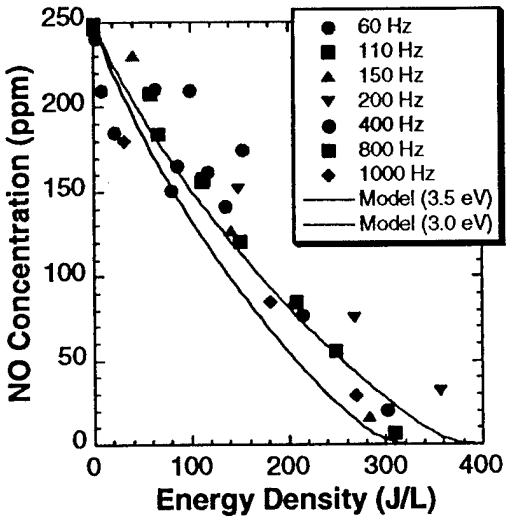

Figure 9. Effect of applied voltage frequency on plasma processing of 250 ppm NO in N_2.

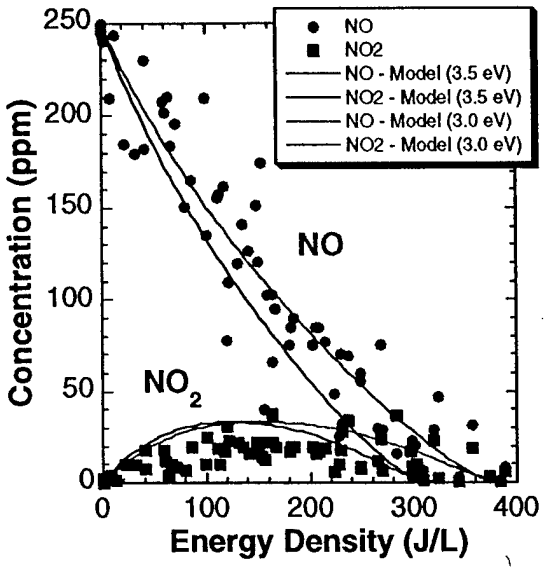

Figure 10. Summary of data on plasma processing of 250 ppm NO in N_2.

EFFECT OF INITIAL NO CONCENTRATION

The results of other experiments on the NO-N_2 mixture using different initial NO concentrations are shown in Figures 11 and 12. These data consistently agree with calculations of the energy consumption for NO_x reduction based on an electron mean energy in the plasma of 3.0 – 3.5 eV.

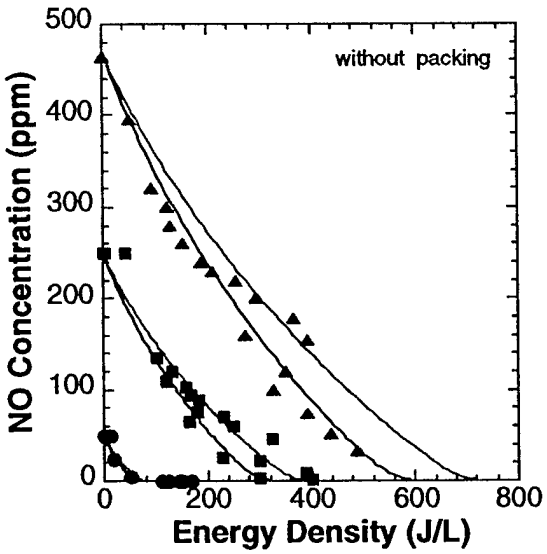

Figure 11. Effect of initial NO concentration on plasma processing of NO in N_2. No packing in the plasma reactor.

EFFECT OF REACTOR GEOMETRY

The data presented here were obtained using dielectric-barrier discharge reactors consisting of concentric tubes.

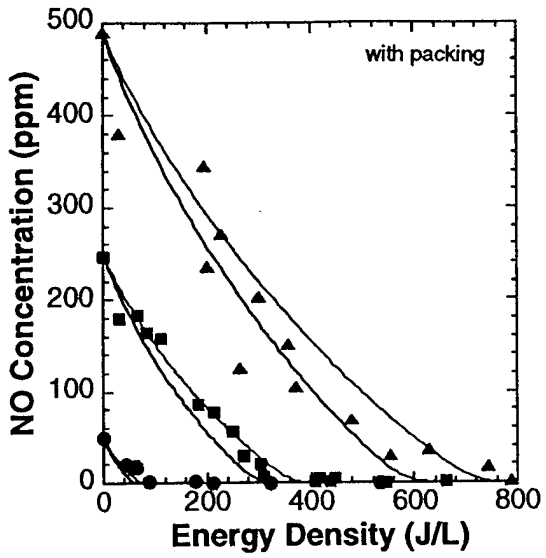

Figure 12. Effect of initial NO concentration on plasma processing of NO in N_2. With glass wool packing in the plasma reactor.

Penetrante et al. [4] has shown that there is no significant difference in the performance of planar and cylindrical reactors.

CONCLUSIONS

Experimental results on plasma processing of NO in N_2 have been presented. The data have been obtained using different packing materials, electrode diameter, and voltage frequencies. We have shown that the applied voltage is not the relevant parameter when comparing the performance of different plasma reactors. Comparisons based on the applied voltage lead to erroneous conclusions. The important control parameter is the energy density delivered to the plasma.

We have found that reactor design has little influence on the basic energy consumption of the plasma. Consequently, different reactor designs should yield basically the same plasma chemistry if the experiments are performed under identical gas composition and temperature conditions.

ACKNOWLEDGMENT

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