sociation of NO molecules. However, because of the relatively low concentration of NO in the exhaust gas, direct dissociation of NO by the electrons is not probable. The kinetic energy of the electrons is deposited primarily into the major exhaust gas components, $N_2$ and $O_2$.

The physics of electron collisions with the $N_2$ and $O_2$ molecules determines the electrical energy cost for the NOx conversion chemistry. The chemistry in the plasma always start with electron-impact dissociation of the abundant molecules. The efficiency for dissociation of various molecules is determined by the average kinetic energy of the electrons. The average electron kinetic energy is determined by the electron-molecule collision cross section and the electric field experienced by the el

The electrons could lose considerable kinetic energy through reactions, such as the vibrational excitation of $N_2$, which heats up the $N_2$ molecule but does not promote the conversion of NOx. The most useful deposition of electron kinetic energy into $N_2$ and $O_2$ is associated with the production of N and O radicals through electron-impact dissociation:

$$e + N_2 \rightarrow e + N(^4S) + N(^4S,^2D) \quad (1)$$
$$e + O_2. \rightarrow e + O(^3P) + O(^3P,^1 D) \quad (2)$$

where $N(^4S)$ and $N(^2D)$ are ground-state and metastable excited-state nitrogen atoms, respectively, and $O(^3P)$ and $O(^1D)$ are ground state and metastable excited-state oxygen atoms, respectively.

The NOx in the engine exhaust gas initially consist mostly of NO. The ground state atomic nitrogen, $N(^4S)$, is the only species produced by the plasma that can lead to the gas-phase chemical reduction of NO:

$$N(^4S) + NO \rightarrow N_2 + O \quad (3)$$

The gas-phase chemical reduction of NOx is therefore determined by the electron-impact dissociation of $N_2$.

## COLLISION CROSS SECTION

The electron-molecule collision cross section represents the probability that the molecule will undergo a specific reaction (for example, dissociation) when hit by an electron. The collision cross section is expressed in units of a geometrical cross sectional area, typically on the order of $10^{16}$ $cm^2$. If the electron hits a circular target of this size perpendicular to its path and centered at the molecule, then the reaction occurs. If it misses that area, then the reaction does not occur.

The collision cross section is a fundamental quantity that has been measured by atomic physicists. The cross section for electron collision with a particular molecule is independent of the composition of the exhaust gas. The cross section for electron-impact dissociation of $N_2$ has a maximum that cannot be exceeded regardless of the plasma reactor design or the way the electrical voltage is delivered to the plasma reactor.

Figure 1 shows the cross section for electron impact on $N_2$ leading to neutral atomic nitrogen products [1].

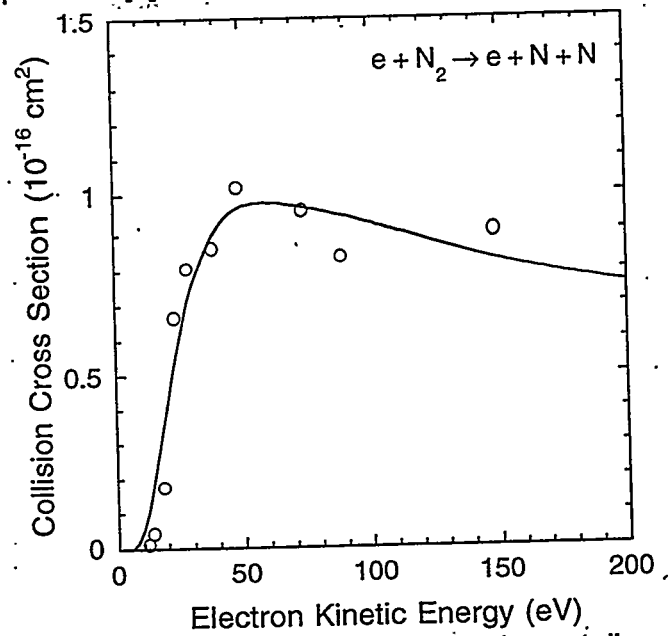


Figure 1. Cross section for electron-impact dissociation of $N_2$.

## ELECTRIC FIELD

There are basically only two types of non-thermal plasma reactors: discharge and electron beam. Discharge plasma reactors are those reactors in which the high voltage elec-

trodes are immersed in the atmospheric-pressure gas stream. The attainable electron kinetic energy in this kind of reactor is very limited. The electrons collide rapidly with the background gas molecules and therefore cannot be accelerated to very high kinetic energies. Electron beam plasma reactors are those reactors in which the high voltage electrodes are in vacuum. The electrons are accelerated in thevacuum region before they are injected into the exhaust gas stream.

The electric field in a discharge plasma is determined largely by the electrical breakdown threshold. Under atmospheric-pressure conditions, the electric field experienced by the discharge plasma is between 30 and 60 kWcm [2], as shown in Figure 2.

Because of the limited range of electric fields that the electrons experience inside a discharge plasma, the average kinetic enrgy that the electrons can attain is also very limited.

Figure 3 shows the average electron kinetic energy as a function of the electric field. All discharge plasma reactors have average electron kinetic energies of 3 to 6 eV [3].

## ELECTRICAL ENERGY COST

For now let us assume an ideal condition in which the plasma is not producing oxidative radicals. Let us further assume that all nitrogen atoms (labeled simply as N) are used entirely for the reduction of NO:

$$N + NO \rightarrow N_2 + O$$

In this case the electrical energy required to reduce NO is simply determined by the electrical energy required to produce N from the electron-impact dissociation of $N_2$. What is the energy required to implement this reduction scheme?

The electrical energy cost for the dissociation of $N_2$ is proportional to the average electron speed and inversely proportional to the dissociation rate. The average electron speed, known as the electron drift velocity, is a balance between energy gain because of electron acceleration

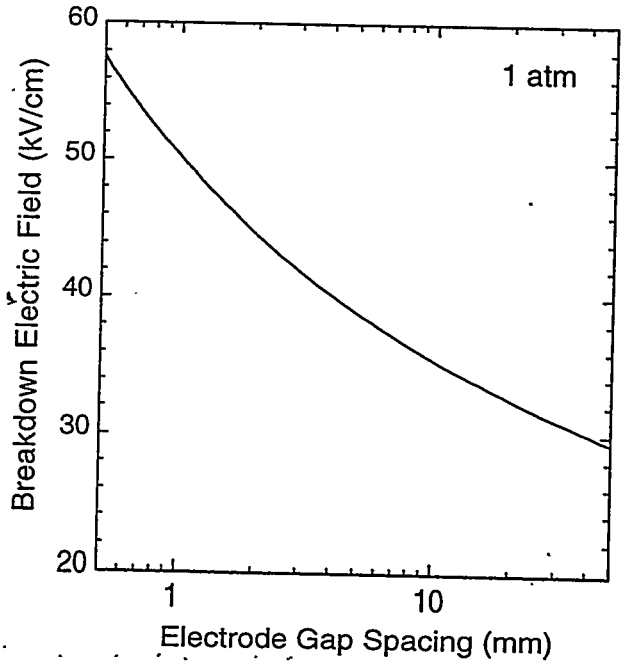


Figure 2: . Breakdown electric field in an atmospheric-pressure discharge plasma.

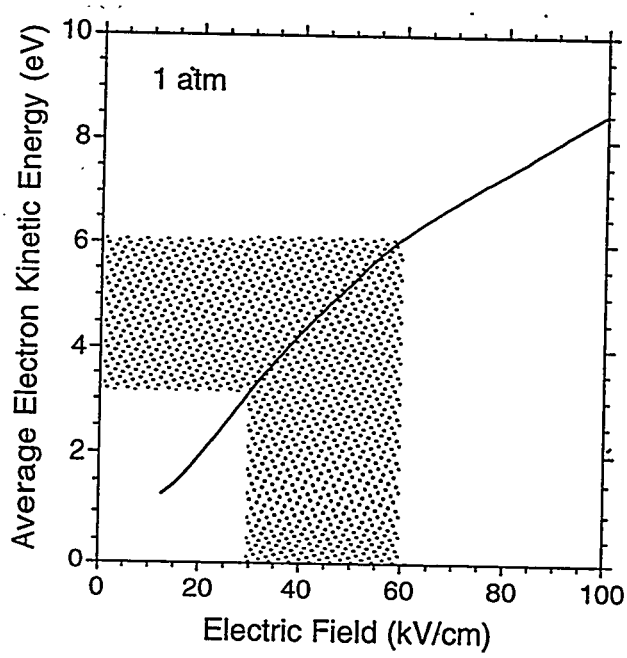


Figure 3. Average electron kinetic energy as a function of the electric field in an atmosphericpressure discharge plasma.

by the electric field and energy loss because of electron collisions with the molecules. Like the average kinetic energy, the drift velocity is determined by the electron-molecule collision cross sections and the electric field.

To minimize the electrical energy cost, one would like to have the highest dissociation rate. The dissociation rate is proportional to the dissociation cross section. The rate for dissociation of $N_2$ has a maximum because of the maximum in the cross section for electron-impact dissociation of $N_2$. The minimum electrical energy consumption for dissociation is determined by the maximum rate for dissociation.

The electrical energy cost can be expressed as a function of the electric field or the average kinetic energy of the electrons in the plasma. Figure 4 shows the electrical 'energy cost for N atom production as a function of the average electron kinetic energy. The electrical energy cost for NOx reduction by reaction (4) is equal to that for N atom production.

The electrical energy cost is very sensitive to the speed of the electrons. For most discharge plasma reactors the average electron kinetic energy is 4 eV [3]. In this case the electrical energy cost for NOx reduction is around 240 eV per NOx molecule. This means that if the plasma uses 5% of the engine energy output, then the amount of NOx that can be removed is $[0.05 / (240 \times 7.8\times10^{-4})] = 0.27$g(NOx)/bhp-hr. To remove 2g(NOx)/bhp-hr, the plasma would need at least 37% of the engine's output energy!

Fast electrons are required to minimize the electrical energy cost for NOx reduction. There are many proposals on how the electron kinetic energy can be increased. For the sake of establishing a fundamental limit, let us assume that a very high electron kinetic energy can be achieved in practice. As shown in Figure 4, the minimum electrical energy cost is 40 eV per NOx molecule [4]. Under this condition, the plasma can chemically reduce 1.6g(NOx)/bhp-hr when 5% of the engine output energy is delivered to the plasma.

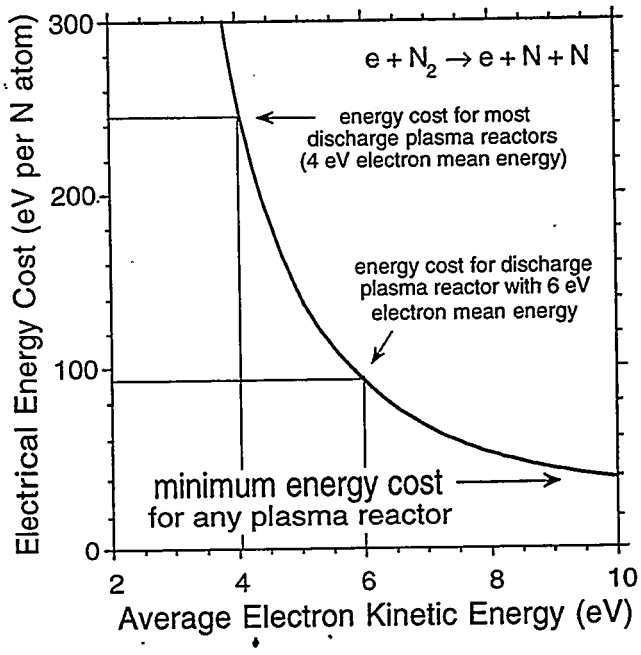


Figure 4. Electrical energy cost for N atom production as a function of the average electron kinetic energy.

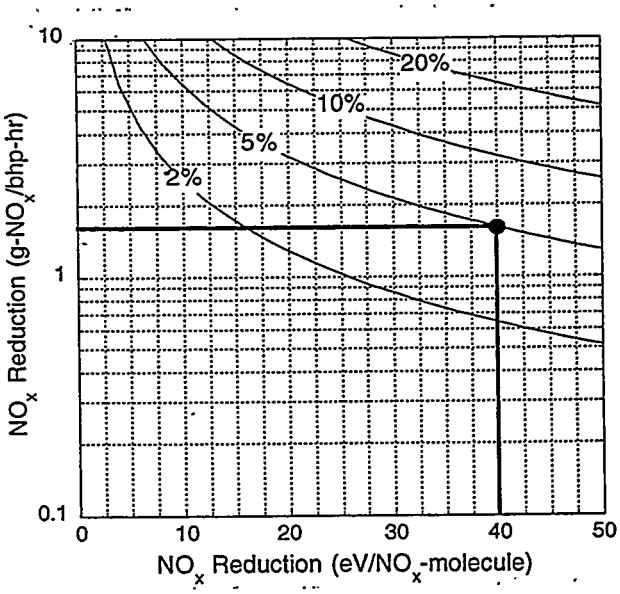


Figure 5: Conversion curves between eV per Nox molecule to give g(NOx)bhp-hr. The curves correspond to different percents of engine output energy aplied to the plasma. The value of 40 eV per NOx molecule is the minimum electrical energy cost for gas-phase chemical reduction of NOx in a plasma. This energy cost corresponds to a maximum NOx reduction of 1.6 g(NOx)bhp-hr when 5% of the engine output energy is applied to the plasma.

## EFFECT OF OXYGEN

It is much easier and cheaper for the electrons to dissociate $O_2$ compared to $N_2$. The dissociation of $O_2$ will produce only oxidative radicals. With $O_2$ concentrations of 5% or more, a significant fraction of the electrical energy delivered to the plasma is dissipated in the dissociation Of $O_2$. The ground state oxygen atoms, 0(3P), convert NO to $NO_2$:

$$O(^3P) + NO + M \rightarrow NO_2 + M \quad (5)$$
$$O(^3P) + O_2 + M \rightarrow O_3 + M \quad (6a)$$
$$O_3 + NO \rightarrow NO_2 + O_2 \quad (6b)$$

Reactions (5) and (6) convert NO to $NO_2$ and leave the same amount of NOx.

During the dissociation of $O_2$, a significant fraction of the atomic oxygen products is in the excited state. This metastable excited-state atomic oxygen, $O(^1D)$, reacts with $H_2O$ to produce OH radicals. The OH radicals convert NO and $NO_2$ to nitrous acid and nitric acid, respectively. Acid products in the plasma can easily get adsorbed on surfaces in the plasma reactor and in the pipes. When undetected, the absence of these oxidation products is often mistaken for chemical reduction of NOx.

In the presence Of $O_2$, not all of the N atoms resulting from the dissociation of $N_2$ lead to the reduction of NO. Dissociative excitation of $N_2$ contributes a large fraction to the total $N_2$ dissociation [5]. A significant species produced by dissociative excitation of $N_2$ is the long-lived metastable, $N(^2D)$. For fast electrons, over half of the total N atoms produced are in the excited metastable states. The rate constants characterizing the interaction of the metastable species N(2D) with various gases are large [6]. In the treatment of NO, there are two competing reactions involving the N(2D) metastable species:

$$N(^2D) + NO \rightarrow N_2 + O \quad (7)$$
$$N(^2D) + O_2 \rightarrow NO + O \quad (8)$$

With 500 ppm NO and 10% $O_2$, the N(2D) species is twenty times more likely to react with $O_2$ than with NO. This means that N(2D) is consumed in the production of NO rather than in the reduction of NO. Whereas the reaction of ground state N atoms, N(4S)' with $O_2$ can proceed only at very high temperatures, the reaction of excited N atoms, N(2D), with $O_2$ can proceed even at room temperature. Since almost half of the total N atoms produced in the plasma are in this excited state, the reduction of NO by the ground state N atoms is almost completely counterbalanced by the production of NO by the excited N atoms. What is left in terms of NOx conversion chemistry is the oxidation of NO to $NO_2$

## HETEROGENEOUS REACTIONS

What we have examined in this paper is the gas-phase chemical reduction of NOx. Heterogeneous reactions in the plasma reactor can also take place. Absorption of $NO_2$ and nitric acid on particulates and reactor walls are often mistaken for gas-phase chemical reduction. There may be conditions in which one can take advantage of plasma oxidation products as intermediaries for the heterogeneous chemical reduction of NOx.

## CONCLUSIONS

The gas-phase chemical reduction of NOx in a plasma can be accomplished via reaction with atomic nitrogen. Under the best condition, the plasma can chemically reduce 1.6 grams of NOx per brake- horsepower-hour when 5% of the engine output energy is delivered to the plasma. This NOx reduction efficiency is a fundamental limit that cannot be exceeded in the absence of heterogeneous reactions or chemical additives.

Fast electrons are required to optimize the production of atomic nitrogen from electron-impact dissociation of $N_2$- Unfortunately, a large fraction of the atomic nitrogen produced by the fast electrons are in the excited state. In the presence of $O_2$, the excited-state nitrogen atoms lead to the production of NO. Thus the development of plasma reactors that can produce fast electrons is not the key to achieving high NOx reduction efficiency when $O_2$ is present in the exhaust gas.
With the $O_2$ concentrations present in diesel and lean-burn engine exhausts, the dissociation of $O_2$ is the most dominant

dissociation reaction that takes place in the plasma. The dissociation Of $O_2$ promotes the gas-phase oxidation of NO to $NO_2$ and nitric acid, but not the gas-phase reduction of NOx to $N_2$. Absorption of $NO_2$ and nitric acid on particulates and reactor walls are often mistaken for gas-phase chemical reduction of NOx,

## ACKNOWLEDGMENTS

This work was performed at Lawrence Livermore National Laboratory under the auspices of the U.S. Department of Energy under Contract Number W-7405-ENG-48, with support from the Chemical Sciences Division of the Office of Basic Energy Sciences and a Cooperative Research and Development Agreement with Cummins Engine Company.

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