# Towards Ideal NOx Control Technology Using Plasma-Chemical Hybrid Process

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# Introduction (1/2)

- In previous researches, the decomposition of $NO_x$ (NO + $NO_2$) by the plasma alone had practical limitations because it was difficult to convert NO to $N_2$ with low plasma power.
- With increase in the plasma power, significant amount of $N_2O$, $NO_3^-$ and/or $HNO_3$ were generated.
- Our approach is to use
  - plasma process for NO to $NO_2$ oxidation with low power
  - chemical process for $NO_2$ to $N_2$ reduction
    - » $2NO_2 + 4Na_2SO_3 \Rightarrow N_2 + 4Na_2SO_4$
- The end product, $Na_2SO_4$ is non-toxic water soluble compounds.

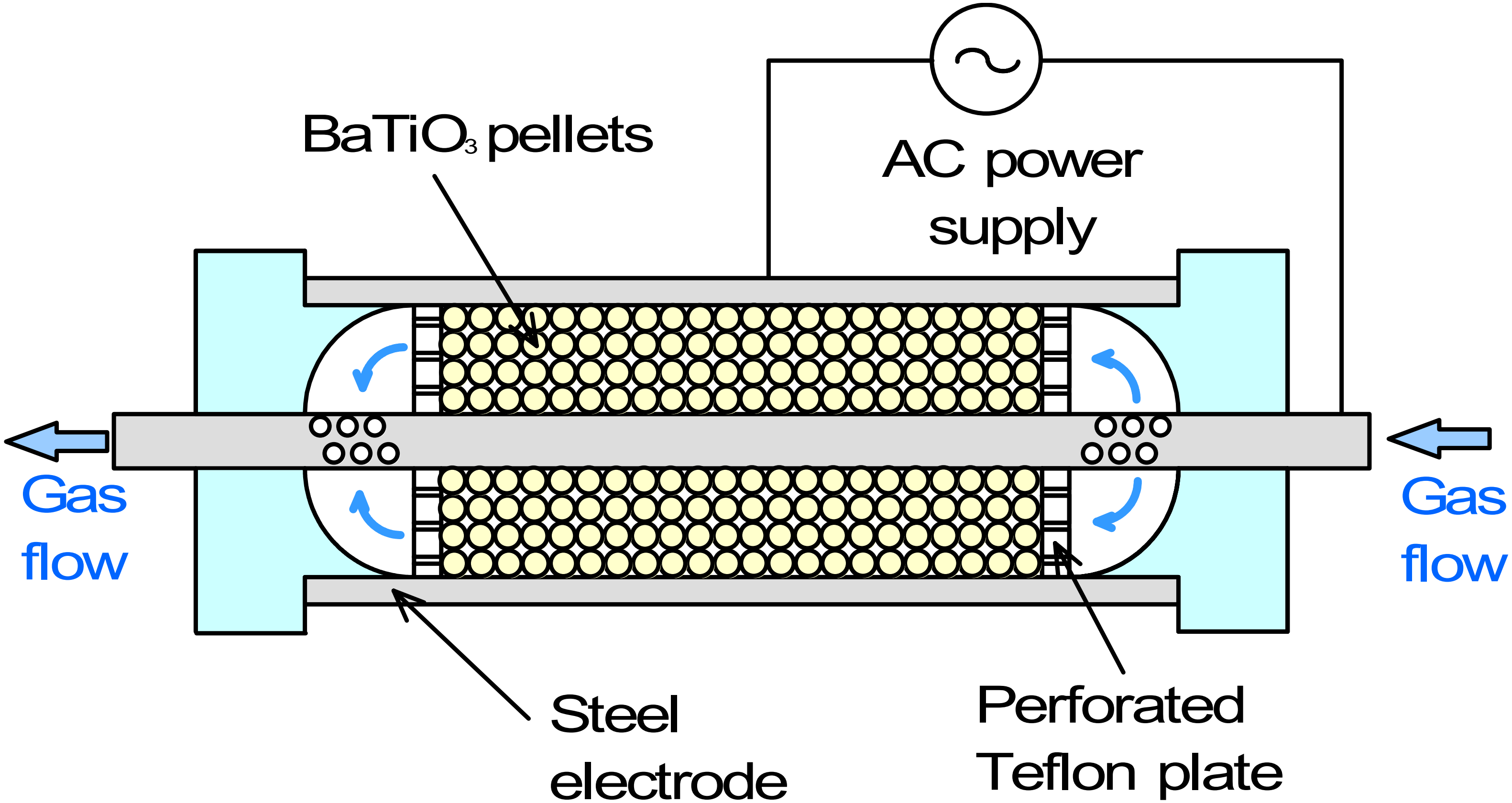
# Introduction (2/2)

- The reaction products such as $HNO_2$ and $HNO_3$ in the chemical process were easily neutralized by, for example, NaOH scrubbing.

- Small amounts of byproducts and lower cost are achieved in this approach.

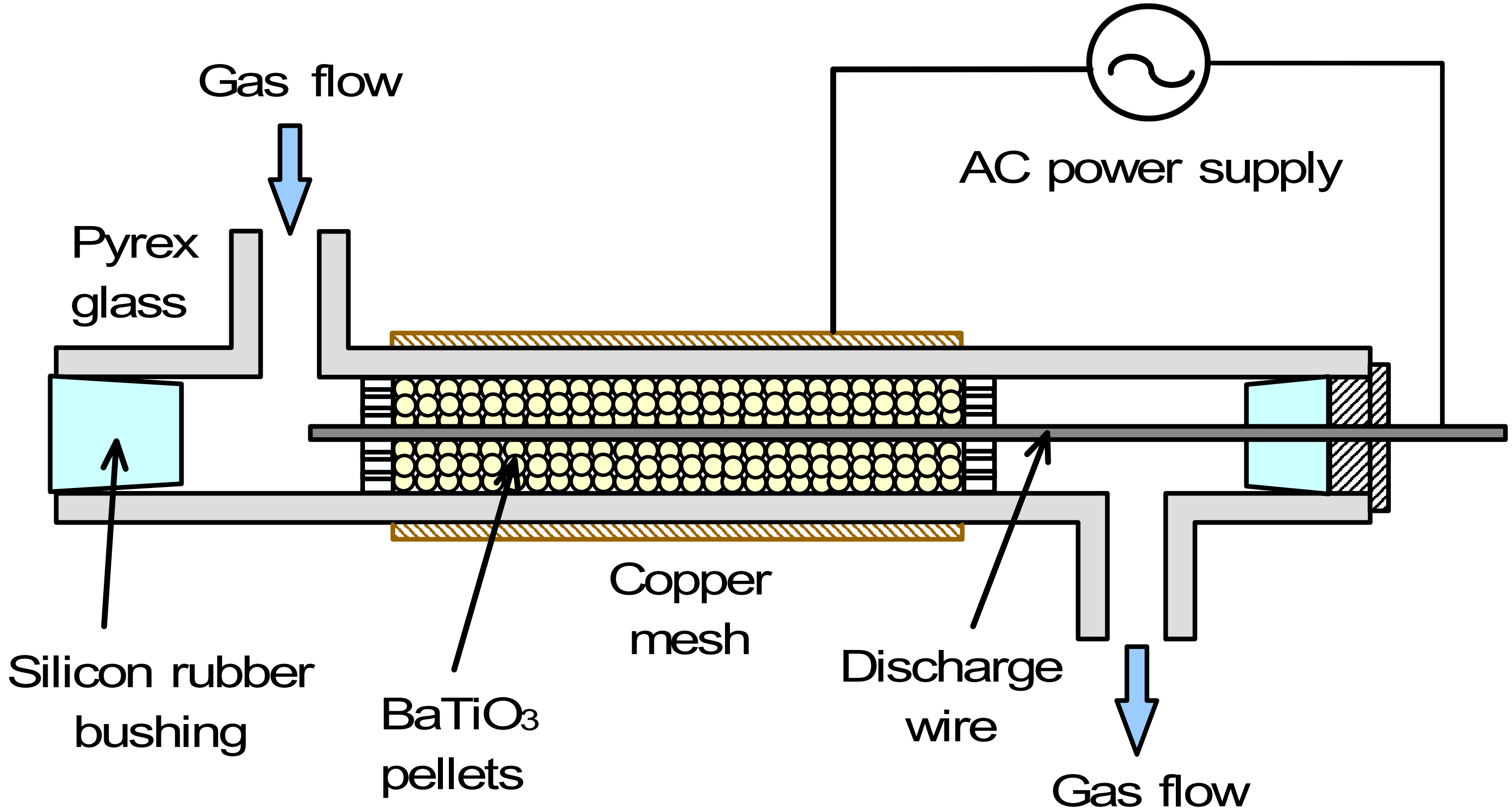
- In the present study
  - Two types of plasma reactors: a traditional packed-bed reactor and a barrier-type packed-bed reactor were investigated. The performances were compared.
  - Reaction byproducts and $NO_x$ removal efficiency were quantified.
  - Almost 100% $NO_x$ removal with negligible CO and $N_2O$ formation was achieved.

# Traditional packed-bed plasma reactor



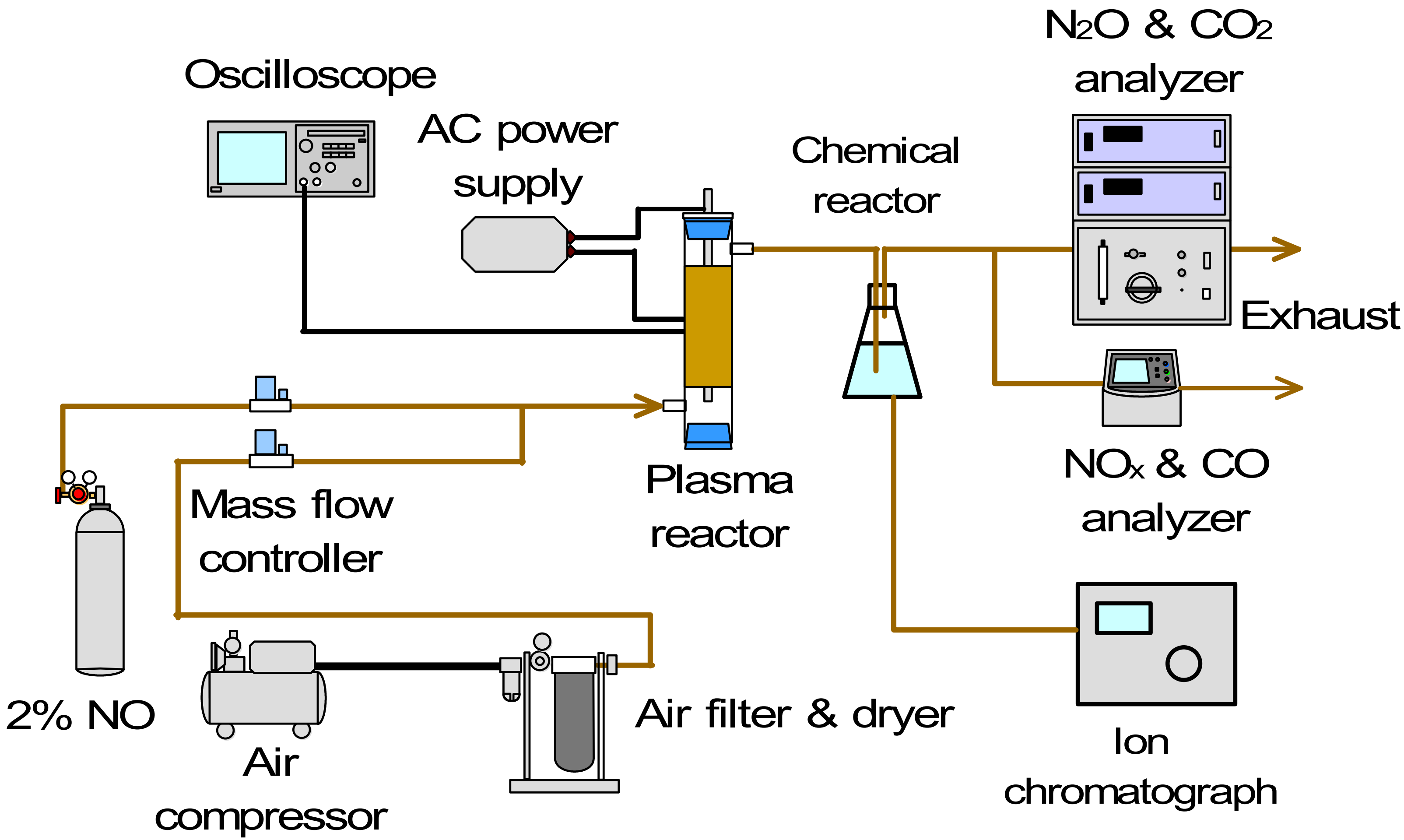

- $d_{in}$=16.6 mm, $d_{out}$= 47.3 mm, $L_{eff}$ = 127 mm
- AC power supply: 60 Hz, 8 kv, 30 mA
- $BaTiO_3$ pellets: $\varepsilon$ =10000, $d$=1 mm

# Barrier-type packed-bed plasma reactor

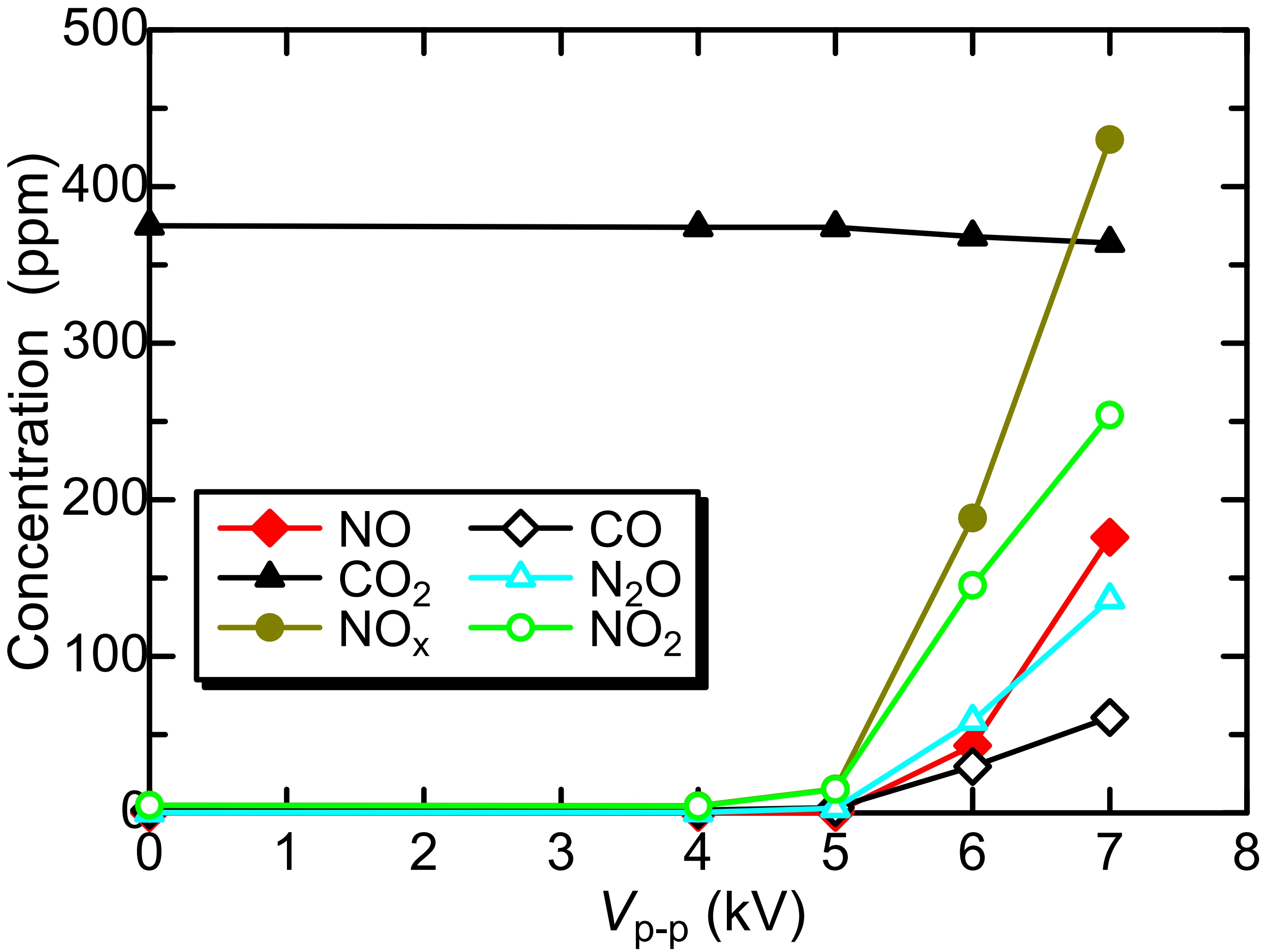



– $d_{in}$=5.0 mm, $d_{out}$= 25.0 mm, $L_{eff}$ = 270 mm
– AC power supply: 60 Hz, 16 kv, 30 mA
– $BaTiO_3$ pellets: $\varepsilon$ =10000, d=1.7～2.0 mm

# Experimental set-up

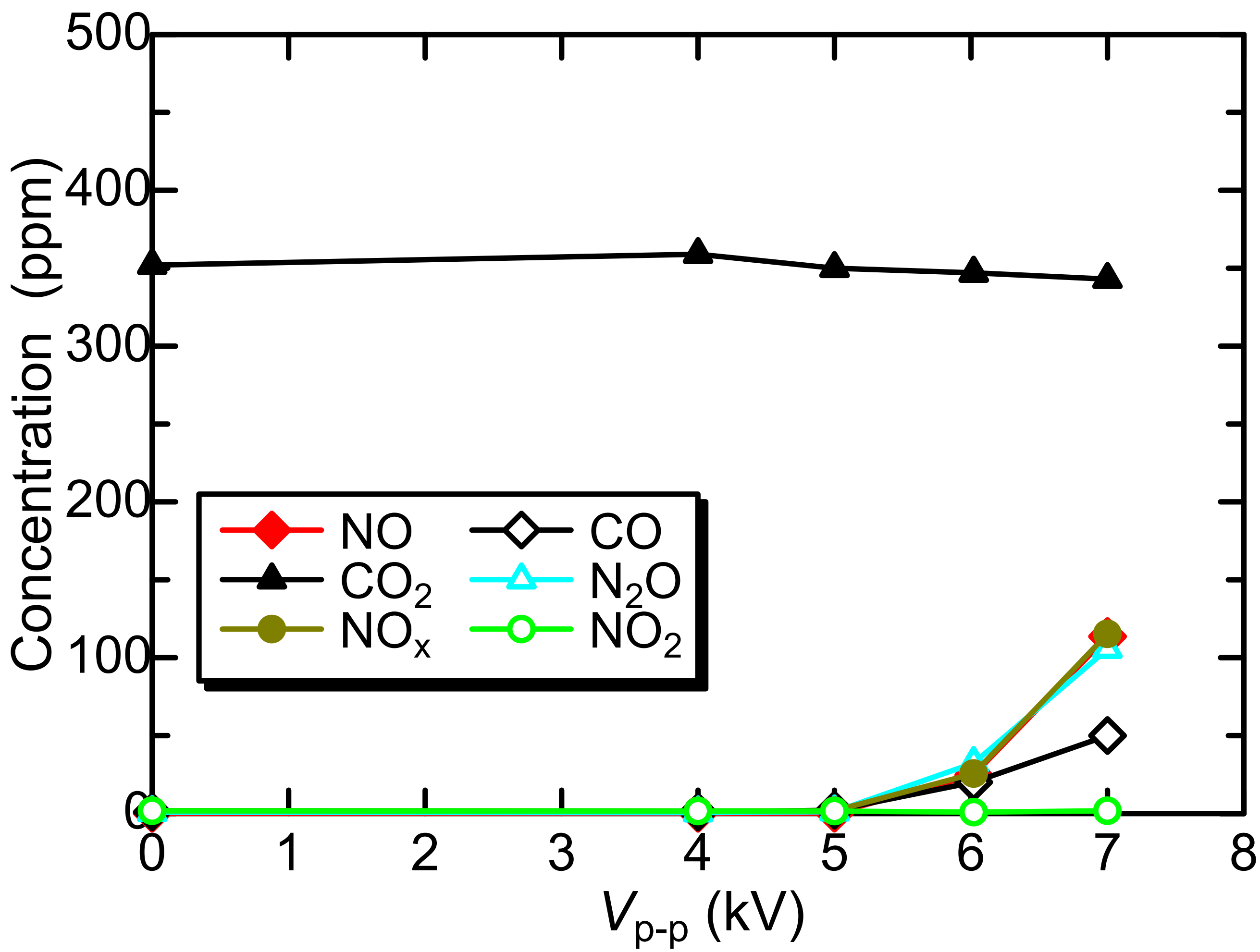


# Decomposition of air
# (Traditional reactor without chemical reactor)



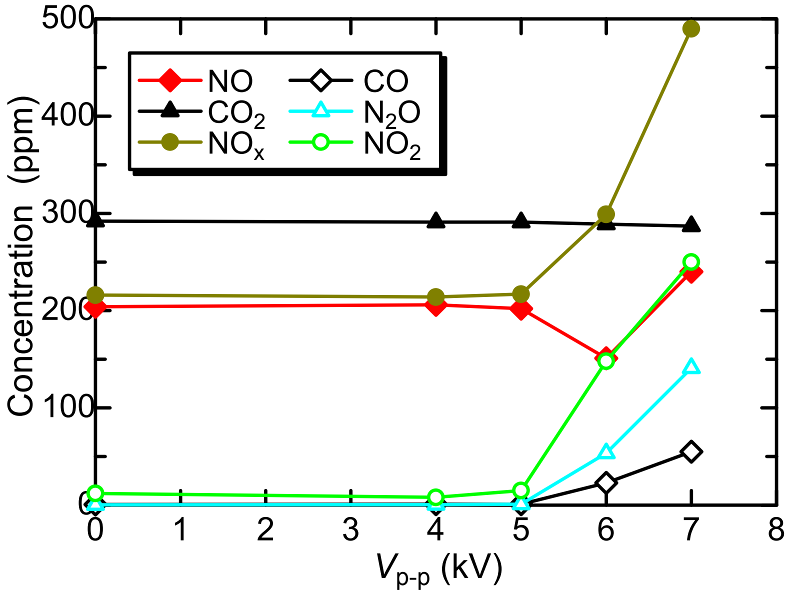

- **Flow rate = 2.0 L/min (Residence time in the reactor is 2.6 s)**

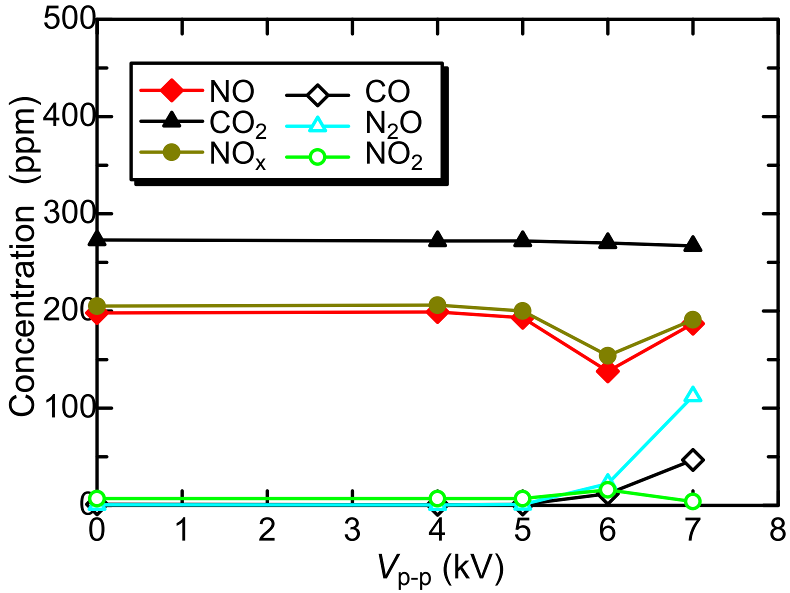
# Decomposition of air
# (Traditional reactor with chemical reactor)




- **Flow rate = 2.0 L/min (Residence time is 2.6 s)**

# Decomposition of 200 ppm NO (Traditional plasma reactor)

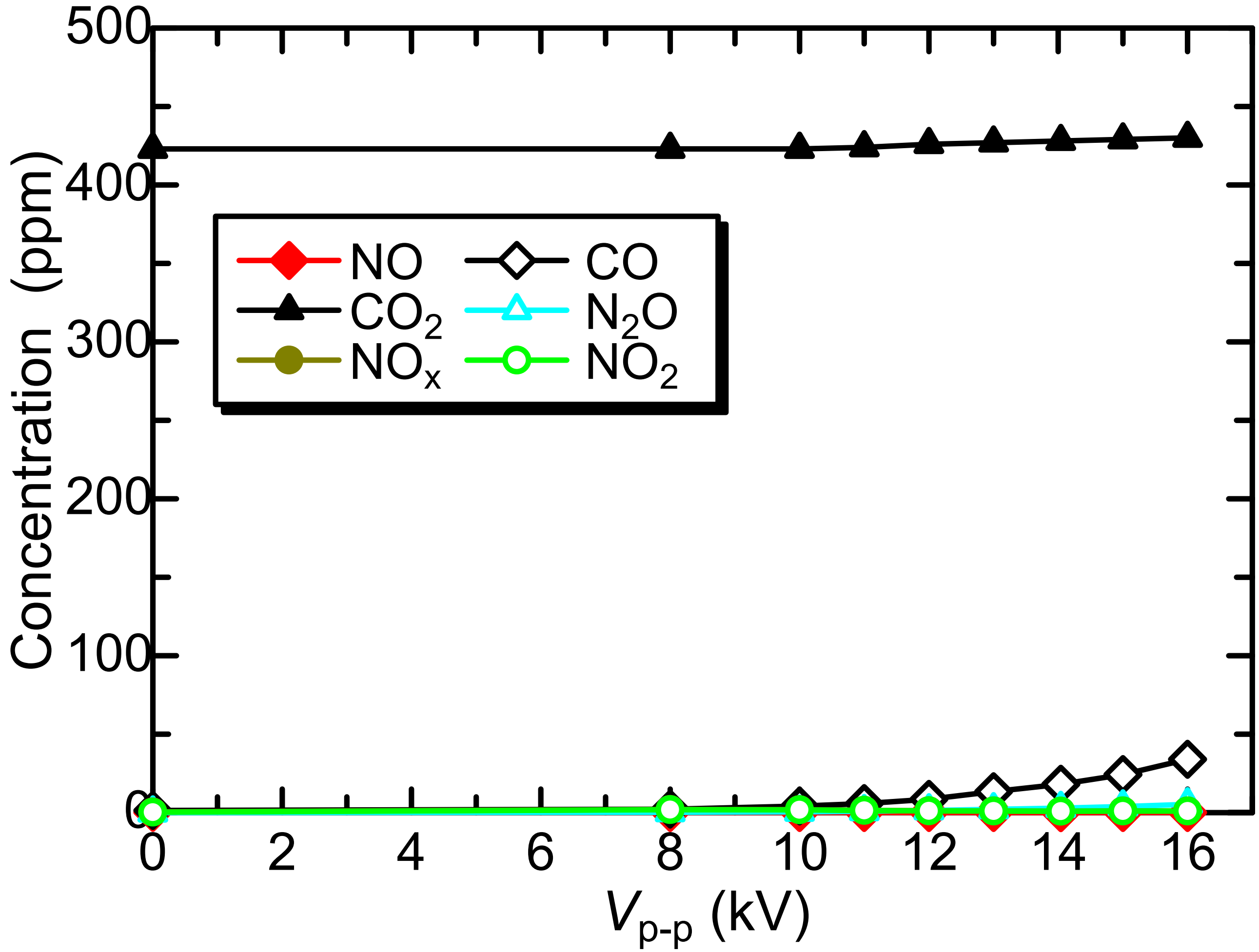



- Without chemical reactor
- With chemical reactor

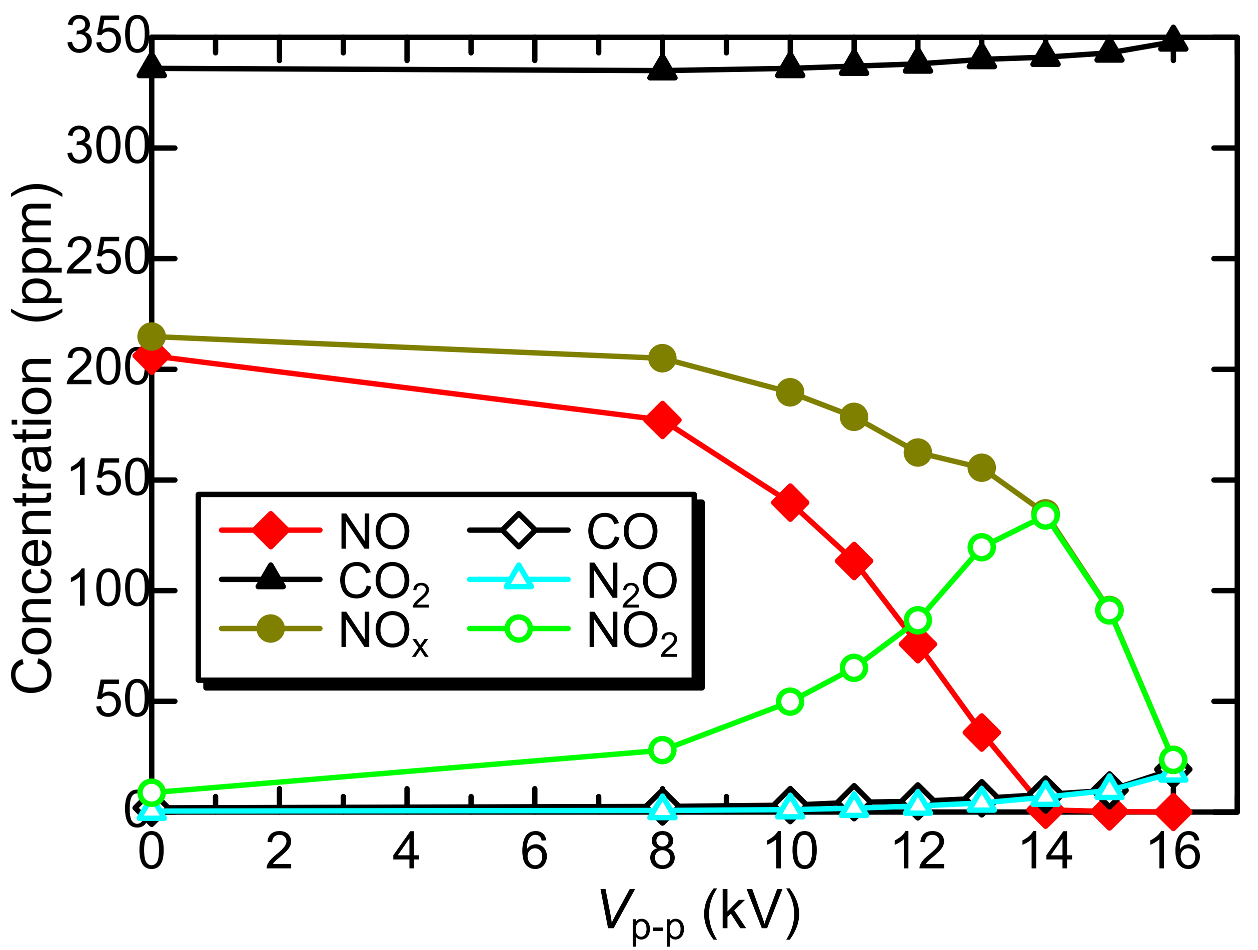
- **Flow rate = 2.0 L/min (Residence time is 2.6 s)**

# Decomposition of air (Barrier-type reactor without chemical reactor)



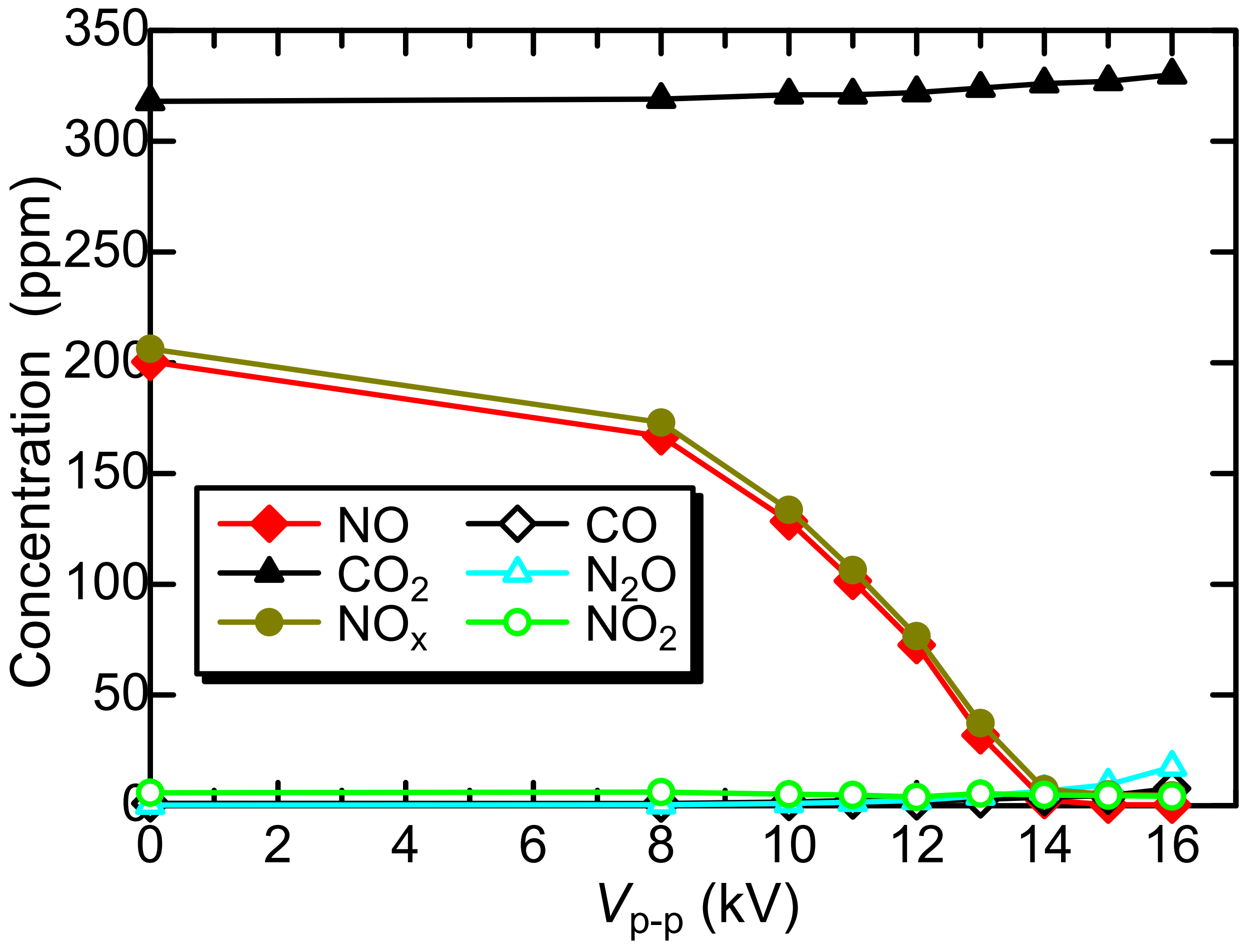

- Flow rate = 2.0 L/min (Residence time is 1.7 s)

# Decomposition of 200 ppm NO (Barrier-type reactor without chemical reactor)




- **Flow rate = 1.0 L/min (Residence time is 3.3 s)**

# Decomposition of 200 ppm NO (Barrier-type reactor with chemical reactor)

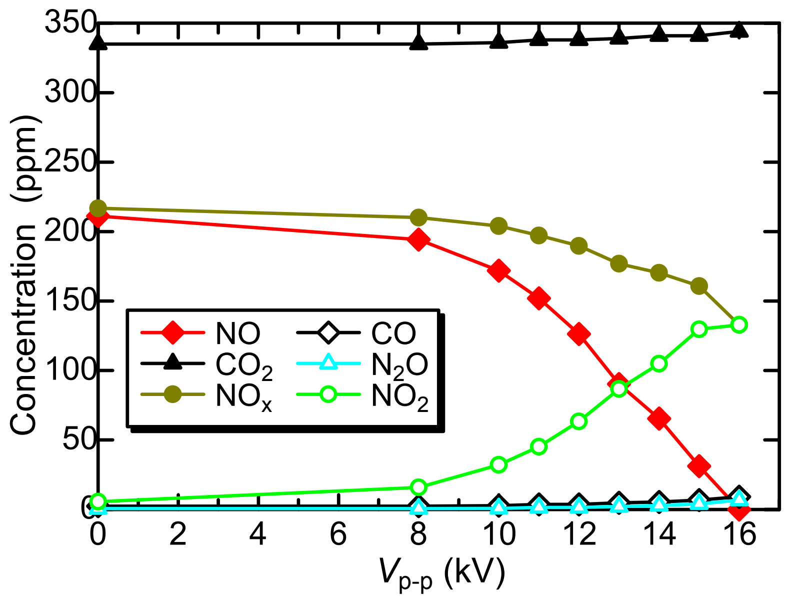



- **All the compounds were disappeared at 14 kV. The $NO_2$ will reacted with $Na_2SO_3$ to form $Na_2SO_4$**

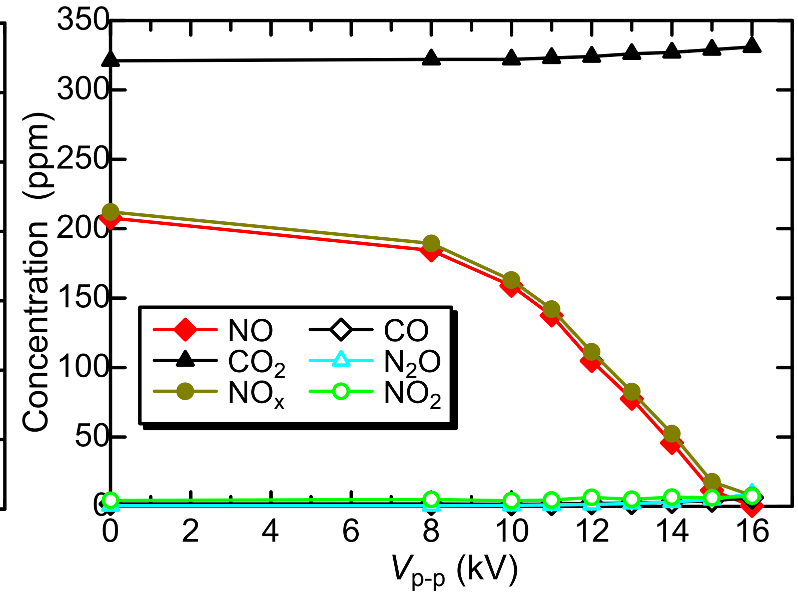
# $NO_2^-$ and $NO_3^-$ ions in chemical reactor

- Ion chromatograph was used to identify the the $HNO_2$ and $HNO_3$ as $NO_2^-$ and $NO_3^-$ ions in 4% $Na_2SO_3$ scrubbing solution and 30 min plasma operation.
- At the applied voltage of 14 kV, the ratio of $NO_2^-$ and $NO_3^-$ was 1.77.
- When the applied voltage was increased to 16 kV, this ratio became 0.57,
- These results indicate that $HNO_2$ and $HNO_3$ exist in the chemical reactor and more oxidation takes place with increasing voltage.

# Decomposition of 200 ppm NO (Barrier-type plasma reactor)



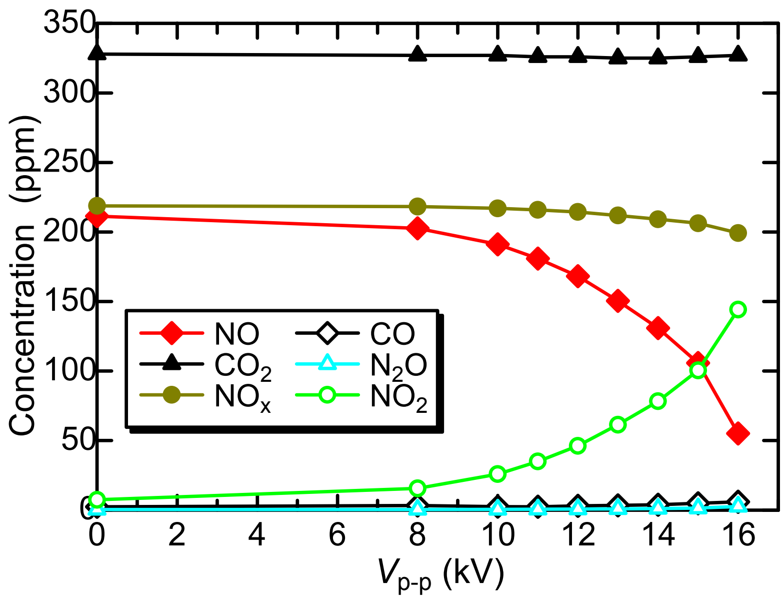

- Without chemical reactor

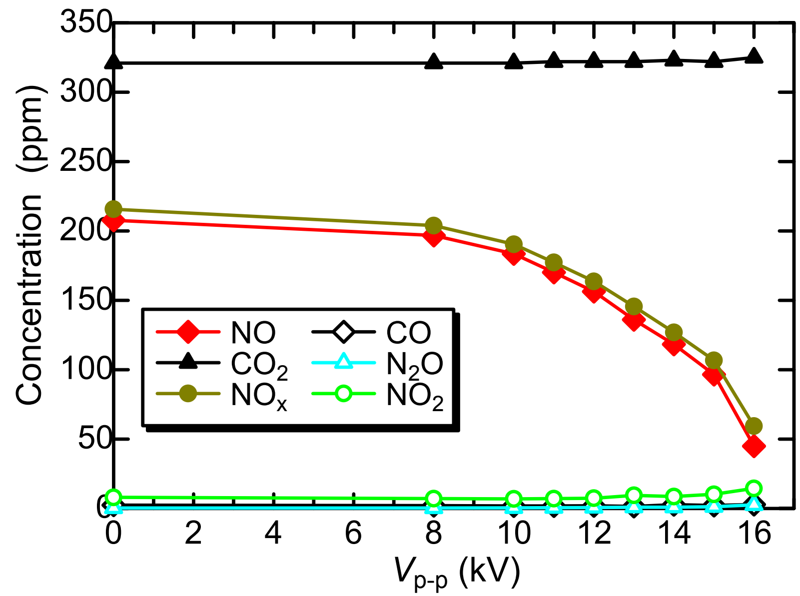



- With chemical reactor

- **Flow rate = 2.0 L/min (Residence time is 1.7 s)**
- **With the chemical reactor, all NO, $NO_2$, $NO_x$, CO, and $N_2O$ reached to near zero at 16 kV.**

# Decomposition of 200 ppm NO (Barrier-type plasma reactor)

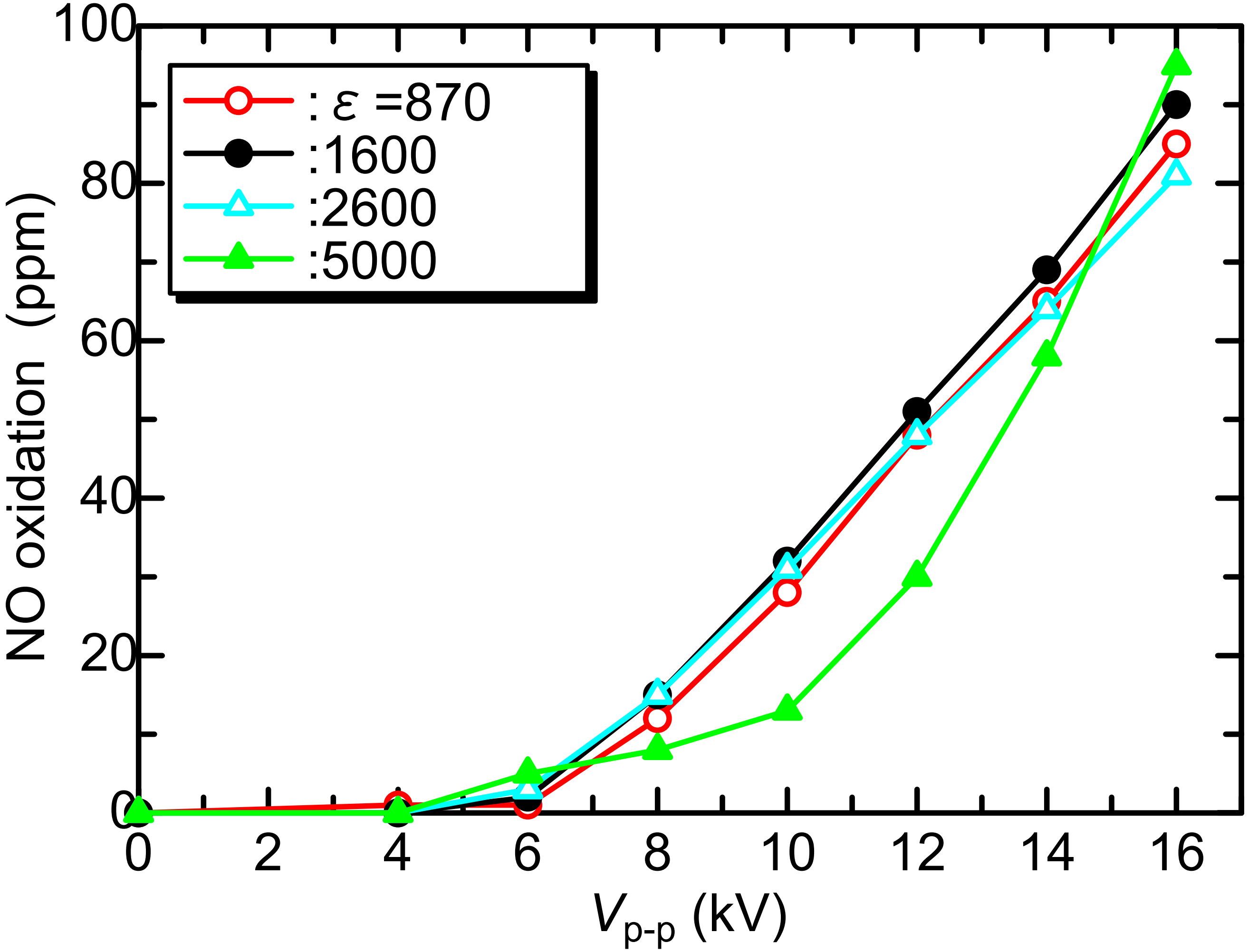


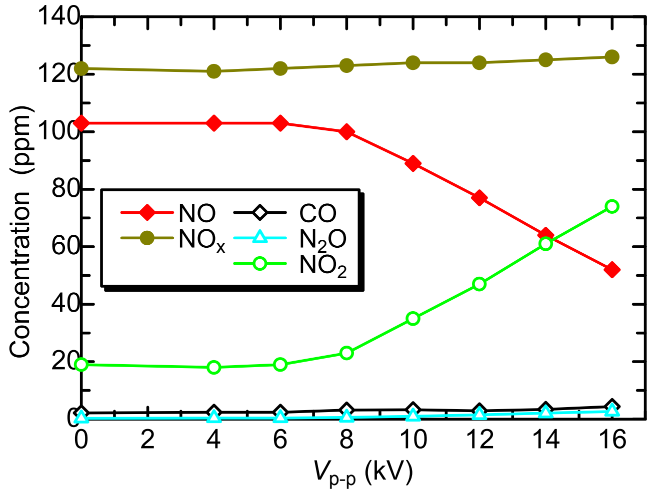

- Without chemical reactor
- With chemical reactor

- **Flow rate = 4.0 L/min (Residence time is 0.8 s)**
- **With the chemical reactor, the NO and NOx was reduced to 50 ppm level.**

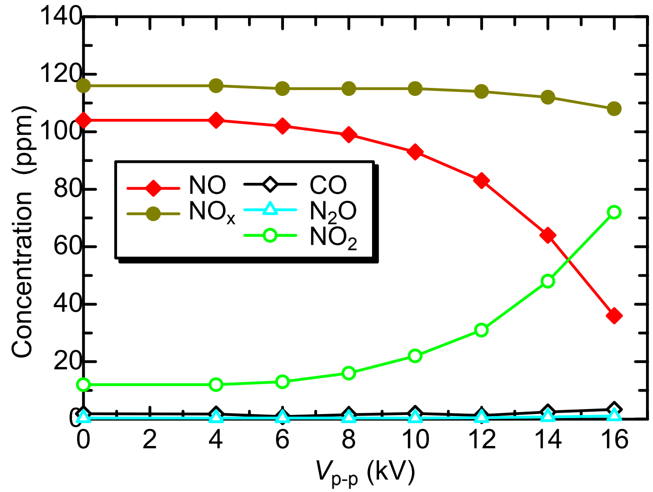
# Effect of pellet's relative dielectric const. on NO oxidation



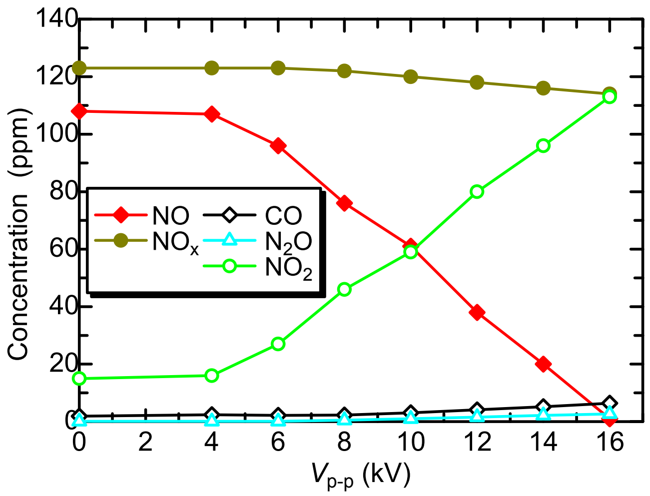
# Effect of pellet diameter on NOx removal




- Pellet diameter=1.0 mm

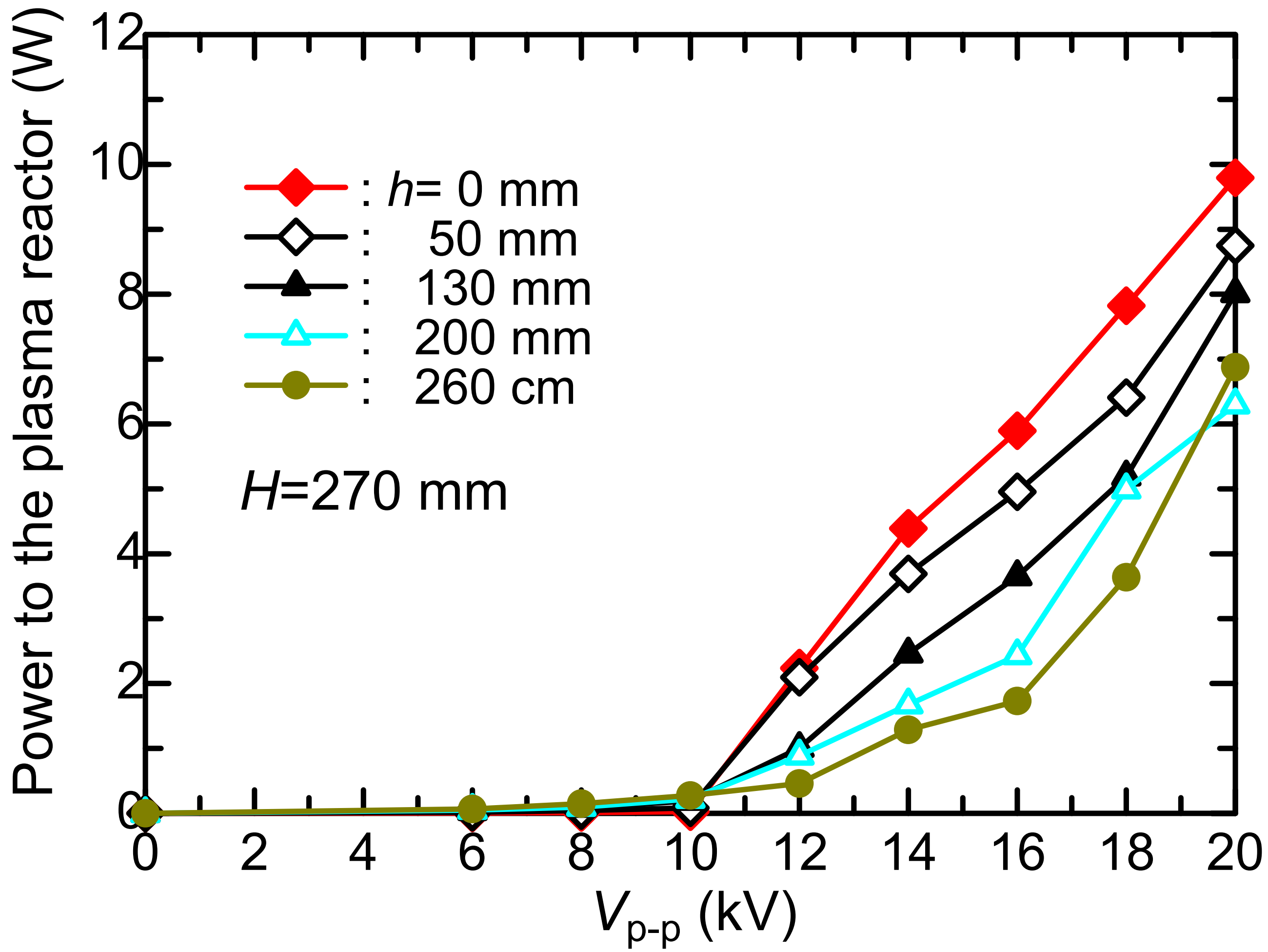



- Pellet diameter=2.0 mm




- Pellet diameter=3.0 mm

# Power consumption vs. voltage (Barrier-type plasma reactor)




- **The power consumption for plasma reactor is about 1.5 W at 16 kV. (h=260 cm)**

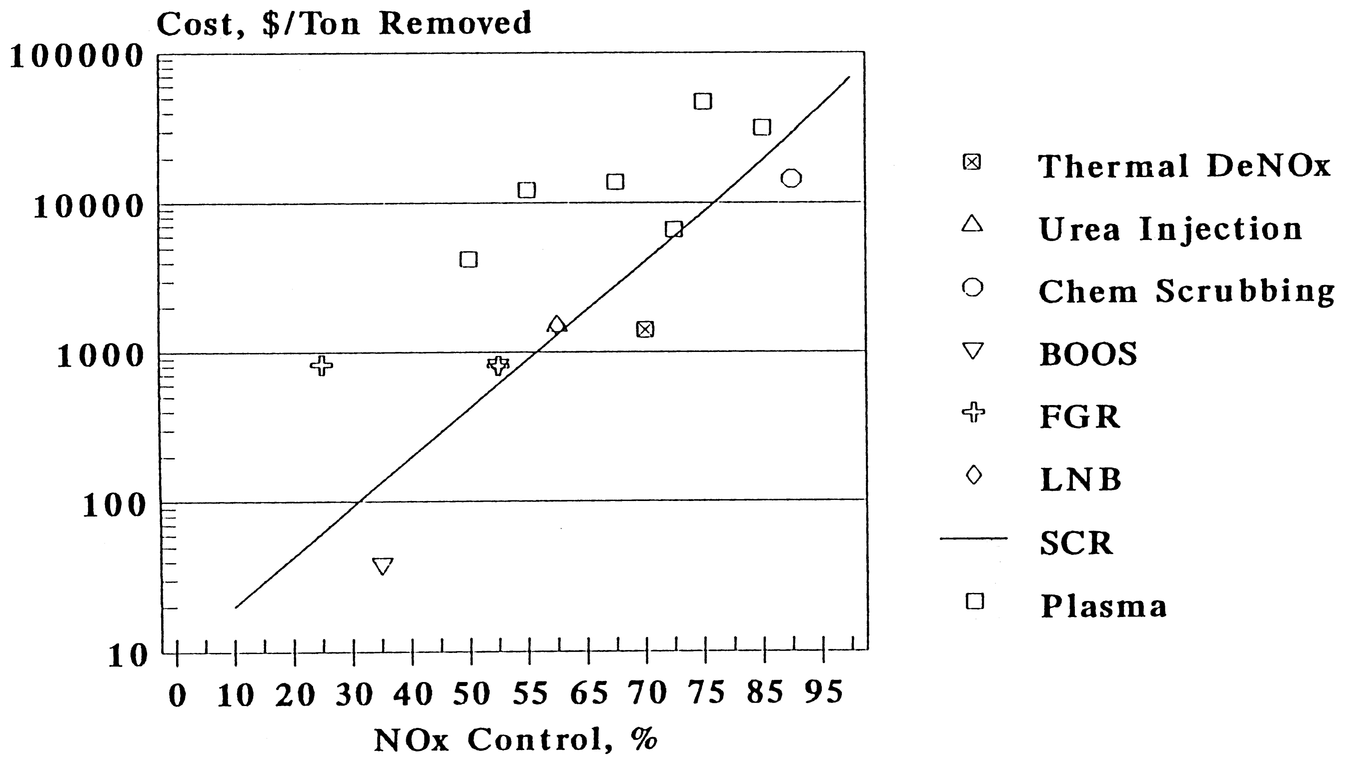
# Total operating cost of the hybrid process

- The specific energy density becomes 43 J/L (*Q*=2.0 L/min)
- **Operating cost for the plasma reactor**
  - **$1,860/ton (1kW=$0.05)**
- **Operating cost for the chemical reactor**
  - **$440/ton ($Na_2SO_3$,1kg=$0.48)**
- **Operating cost for the hybrid process**
  - **$2,300/ton (100% NOx removal)**
- which is more than 15 times economical than the conventional SCR process

# Conclusions

- Two types of the plasma reactors for NOx reduction were investigated and the reaction byproducts (NO, $NO_2$, $NO_x$, CO, $CO_2$ and $N_2O$) were quantified.
  - **The nonthermal plasma should be used for the oxidation from NO to $NO_2$**
  - **The chemical process should be used for the reduction from $NO_2$ to $N_2$**
- The barrier-type plasma reactor is far better than the ordinary plasma reactor, which is able to achieve 100% NOx removal with negligible CO and $N_2O$ formation using the $Na_2SO_3$ chemical reactor.
- The total operating cost becomes $2,300/ton which is more than 15 times economical than the conventional SCR process

# Total operating cost for 100% NOx removal

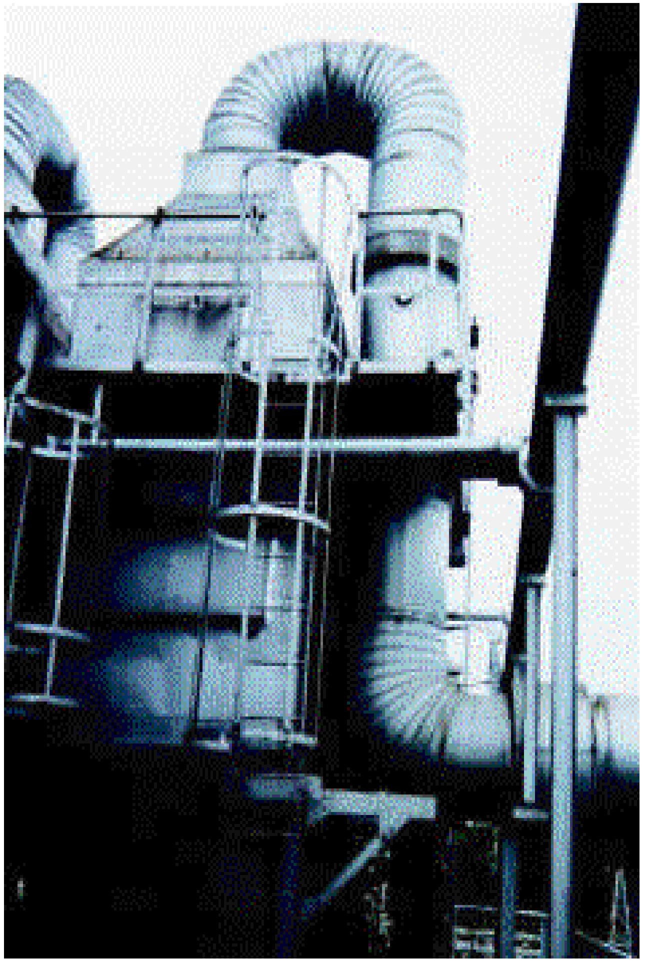



Yang et al, CEC Vol. 143, 1996
Penetrante, B., CRADA Report, 1993
70 - 780 ev/molec

- In this method, 100% NOx removal is possible at the cost $2300/ton
  - Plasma power=1.5W, The cost is $1,860 /ton
  - The price of $Na_2SO_3$ is $440/ton

# SCR（Selective catalytic reduction）法

- 排ガスに含まれる有害な窒酸化物を無害な物質に変え脱硝システム
- SCR法
  - 脱硝装置は反応器（触媒ケース），アンモニア水供給装置，制御装置から構成
  - 自動的にアンモニアは排ガス中へ均一に噴霧
  - それにより、触媒上でのNOxの還元反応をむらなく行わせ、更に未反応なアンモニアが出る事を防ぐ



工場用脱硝システム