ECH/EDP簡介

--- 促進的氮氧化物分解 (PROMOTED NO_X DECOMPOSITION, PND) 轉化器(CONVERTER)裝置

ECH --- ELECTRO-CATALYTIC HONEYCOMB
EDP --- ELECTROCHEMICAL DOUBLE-CELL PLATE
NO_X --- NITROGEN OXIDES

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內燃機燃油效率的緊箍圈
--- NO_X 的排放控制

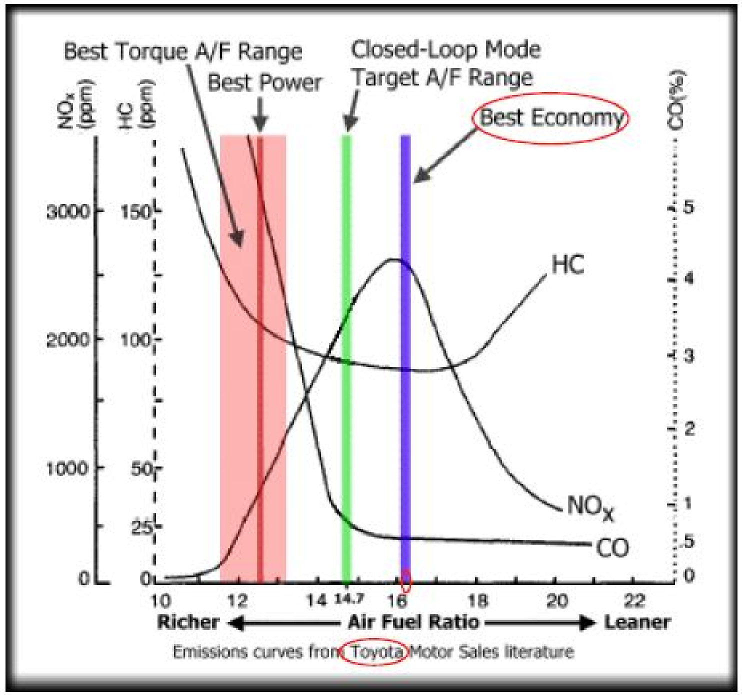
Initiation: $O_2 \rightarrow 2O$
(thermal cracking – providing O for combustion)
Chain reaction: $O + N_2 \rightarrow NO + N$
$N + O_2 \rightarrow NO + O$
Termination: $NO + O \rightarrow NO_2$

- 內燃機燃燒溫度越高 → 燃油效率越高
  - 絕大部份碳氫化合物燃燒轉換成能量
  - 低 CO & HCs (hydrocarbons) & PM (particulate matter)
  - 唯一剩下的問題是高濃度NO_x的排放控制
    - 空氣中 N_2/O_2 ~ 78/21 (V/V)
    - 燃燒溫度越高則 N_2反應成NO_x的濃度越高 (無可避免的宿命—如上右所示的燃燒副反應)
- 柴油汽油車燃油效率是最佳狀態嗎? NO
  - 因為: 目前deNO_X轉化器的效果不佳及諸多操作限制
  - 所以: 為了控制NO_X的排放而犧牲部份的燃油效率(即在較低溫度下操作)
- 你所不知的現況: 犧牲燃油效率換取NO_X排放控制的策略
  - In 汽油車 (見下頁)
    - TWC (Three Way Catalyst)/NSR (NO_X Storage and Reduction)
    - 化學計量燃燒法(A/F =14.7), 控制氧含量而在較低溫燃燒
  - In 柴油車(見下下頁)
    - SCR (Selective Catalytic Reduction)
    - EGR (Exhaust Gas Recirculation)
      - 控制較低溫燃燒及氧含量

目前解決NO_X排放控制策略 --- 汽油車

- 氣/燃比 (air/fuel ratio, A/F): 14.7
  (最經濟的條件應為~16.2, 如右圖所示)
  - 燃油效率較差 (因引擎溫度較低)
  - NO_X 濃度較低
  - CO,HC 濃度較高 (因為燃燒溫度低而無法完全燃燒)
- Three-way catalytic (TWC) converter
  - 引擎需控制 A/F在觸媒轉化器可操作之範圍 --- 此A/F範圍 (A/F window) 窄, 控制複雜
  - 回饋控制造成處理的無法及時而嚴重影響處理效果
  - 低溫下無法操作

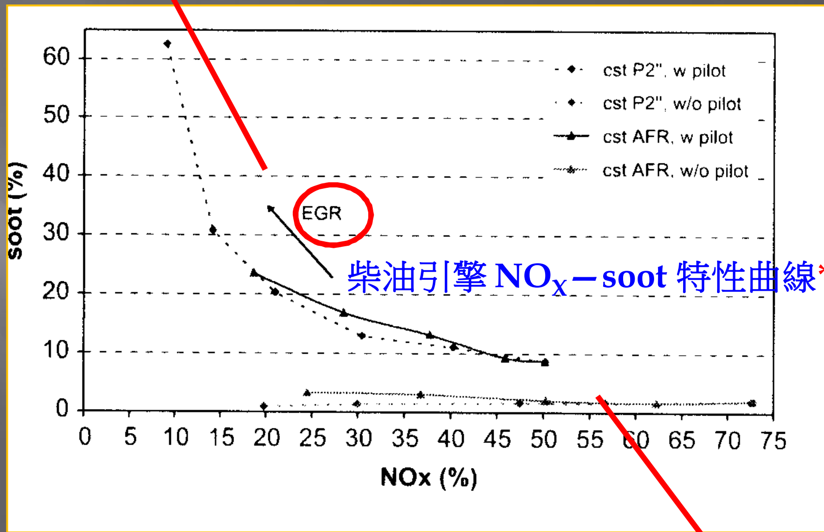
Effect of air-fuel ratio on NO_x emission & fuel economy



目前解決NO_X排放控制策略 --- 柴油車

- 降低引擎燃燒溫度 – EGR (廢氣迴流)
  - 燃油效率較差(因引擎溫度較低)
  - NO_X濃度較低
  - 產生高濃度 soot (需加裝濾煙器, Diesel Particulate Filter, DPF)
- SCR --- 選擇性觸媒還原
  - 需消耗還原劑 (氨水或尿素) 成本高且造成使用者不便
  - 反應會形成 N_2O 溫室氣體
  - 會有未反應完之氨氣二次汙染問題

目前為了降低 NO_X 濃度 → 增加 EGR迴流比例來降低引擎燃燒溫度 → 造成SOOT濃度增加



降低 EGR比例 → 增加引擎燃燒溫度→ 造成 NO_X濃度增加

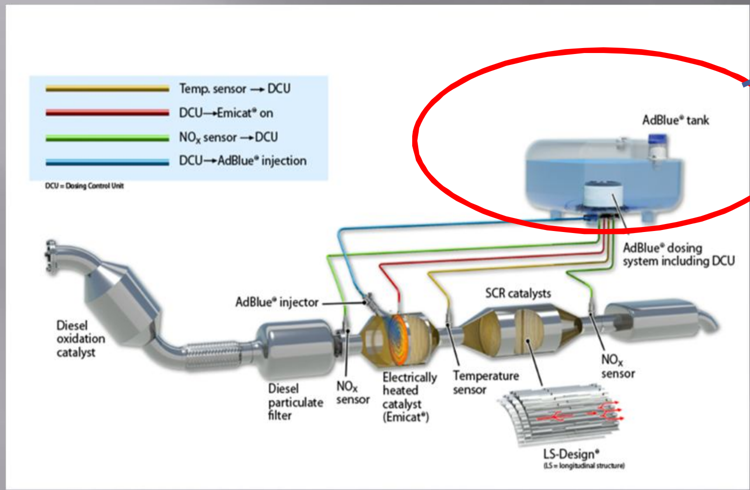
* NO_X-soot trade-off during exhaust gas recirculation (EGR) of diesel engine [Energy 33 (2008) 22]

Diesel exhaust causes cancer (WHO 2012.6.12) Diesel engine exhaust fumes (soot) are a definite cause of **lung cancer**

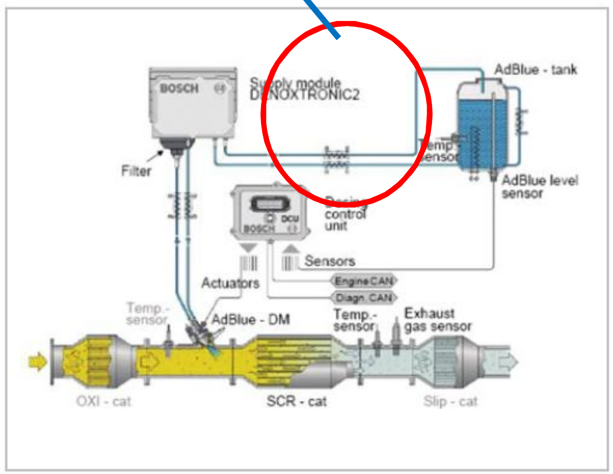
Those very small particulates, which can go through the DPF, can penetrate deep into the lung. [American Lung Association/Calif.]

複雜的 SCR系統

尿素儲存槽

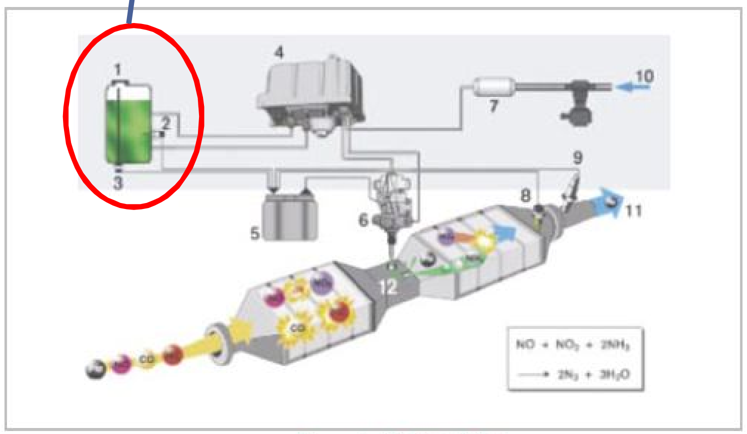


Urea-based **SCR** system for passenger cars

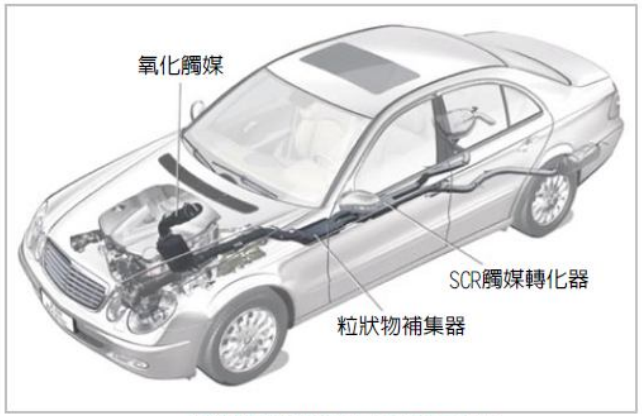


Bosch 輕型柴油車SCR系統

尿素儲存槽



Bosch SCR系統



E320輕型柴油車SCR系統

- SCR系統複雜
- 尿素儲存槽佔去車體內部空間

目前使用於汽車的de-NO_X技術的缺點

- **Three-way catalytic (TWC) converter (honeycomb)**
  - Engine operation must be adjusted to accommodate the exhaust treatment.
  - The usage of precious metals.
  - Stoichiometric burn — low fuel efficiency.
  - Treatment delay -- the catalyst is not effective at ambient temperature and thus a heating period is required. [for all current deNO_X via reduction or storage]
- **Exhaust Gas Recirculation (EGR)**
  - To result in low NO_X concentration in exhaust at the expense of fuel efficiency.
- **Selective Catalytic Reduction (SCR)**
  - The consumption of reducing agents, *e.g., ammonia in urea-based SCR*
    - *costly &* inconvenient refilling
  - The formation of N_2O, a strong greenhouse gas.
- **NO_X Storage and Reduction (NSR) — lean-NO_X trap**
  - The consumption of fuel for NO_X treatment.
  - Limited storage capacity.
- **Electrochemical NO_X Reduction with applied voltage (electrical current)**
  - The consumption of electricity with low current efficiency.

如果有個裝置可在富氧下有效處理 NO_x 汽車業會發生甚事呢?

~~犧牲燃油效率換取NOx排放控制的策略~~

兼俱環保及燃油效能的最佳方案
ECH (Electro-Catalytic Honeycomb)
EDP (Electro-Catalytic double-cell plate)

- 引擎可操作在較高溫而得高效的狀態
  - 若用汽油引擎(火星塞點火)而僅提升氣燃比由現今的14.7提升至16.2，則燃油效率可提高達20 % 。
  - 若將汽油引擎由火星塞點火換為壓縮點火，則燃油效率可提高達50 %。
    [依據美國前能源部長 S. Chu 所述 Nature 488 (2012) 294]

提高燃油效率 50 %

- 控制系統簡化
  - 汽油車: 免除化學計量燃燒的複雜控制
  - 柴油車: 移除EGR及DPF及相關的複雜控制
- 環境保護及人體健康
  - 以前需由氧化觸媒轉化器來減量的 HC, CO (污染物) 在引擎燃燒室中完全轉化成 H_2O, CO_2 及能量 (燃油效能提高)
  - 柴油車不再排放黑煙 → 環保&降低致癌物
  - 高效燃燒 → 溫室氣體減少

符合最新 EURO 6環保法規

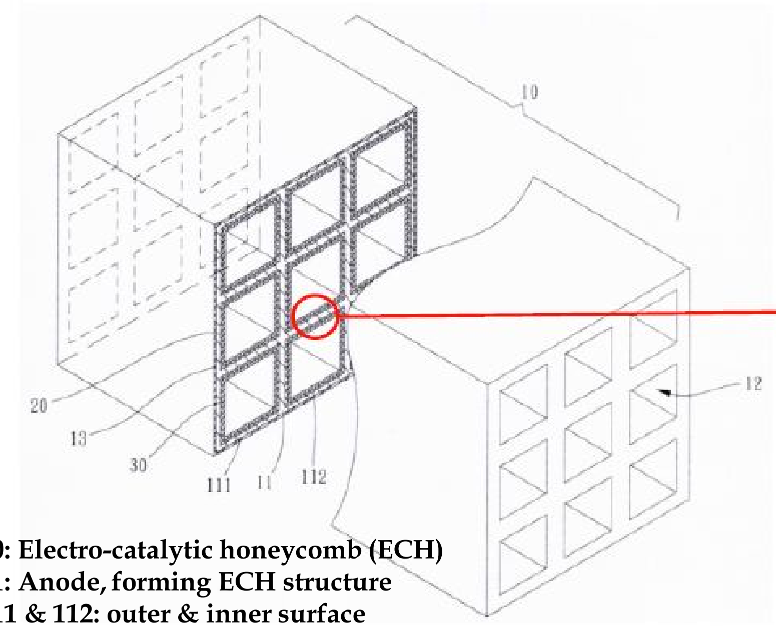
ECH (Electro-Catalytic Honeycomb)

ECH [EU patent granted & other patent applications filed]

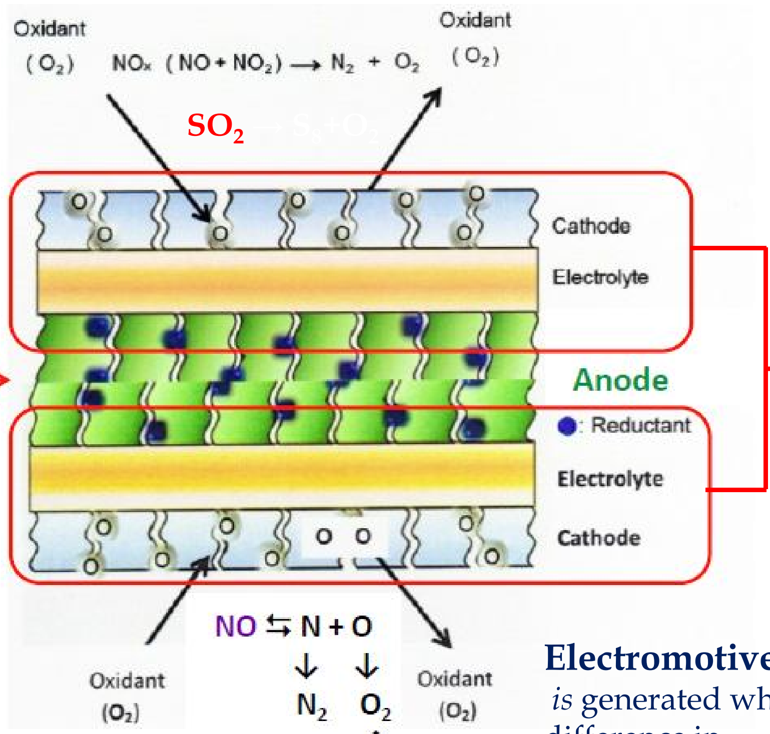
The ECH works on **Promoted NO_X Decomposition (PND) & Promoted SO_2 Decomposition (PSD)**

i.e. emf-promoted ***decomposition of*** *NO_X & SO_2*

$$NO_X\ (NO+NO_2) \rightarrow N_2+O_2 \qquad SO_2 \rightarrow S_8+O_2$$



10: Electro-catalytic honeycomb (ECH)
11: Anode, forming ECH structure
111 & 112: outer & inner surface of the anode structure
12: Exhaust flow channel
13: Shell, covering the outer surface of the anode structure
20: Electrolyte layer, coated on the inner surface of the anode structure
30: Cathode layer, facing the exhaust flowchannel for exhaust treatment



Electrochemical double cell

$NO_2 \leftrightarrows NO + O$

$O_2 \leftrightarrows 2O$

$SO_2 \rightarrow S + 2O$

$S_8 \leftarrow S_2 \quad O_2$

Electromotive force (*emf*): *is* generated when there is a difference in oxidation/reduction potentials of Cathode/Anode and increases with potential difference.

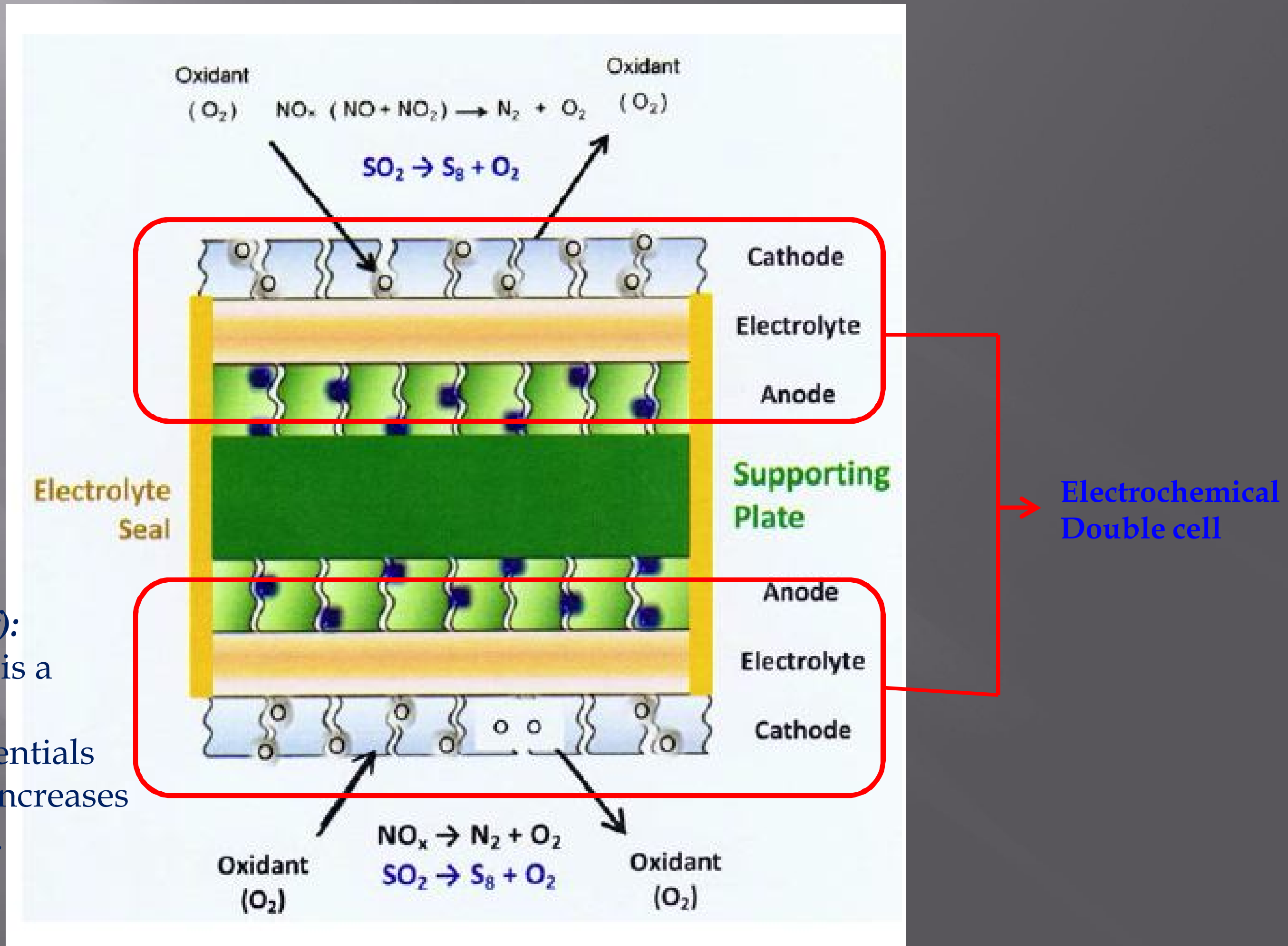
EDP (Electro-Catalytic double-cell Plate)

[patent applications filed]

The EDP works on **Promoted NO_X Decomposition (PND) & Promoted SO_2 Decomposition (PSD)**

i.e. emf-promoted ***decomposition of NO_X & SO_2***

NO_X ($NO+NO_2$) $\rightarrow N_2+O_2$ $SO_2 \rightarrow S_8+O_2$



Electromotive force (*emf*):
is generated when there is a difference in oxidation/reduction potentials of Cathode/Anode and increases with potential difference.

ECH & EDP 富氧下deNO$_X$ 的特性

- No consumption of reducing agent or else
  - Care free
- Higher O_2 concentration results in higher deNO$_X$ rate
  - due to increased promotion with *emf*
  - Simultaneous oxidation of **hydrocarbons, CO** & **Particulate Matter (PM) feasible**
- Higher NO$_X$ concentration can result in higher deNO$_X$ rate [obeying reaction kinetics]
  - Highly fuel-efficient engines
- Relatively constant deNO$_X$ rate at very low NO$_X$ concentration due to a specific reaction mechanism
  - near-**zero NO$_X$ emission can be achieved**
- No temperature window & effective deNO$_X$ from ambient temperature
  - no treatment delay & deNO$_X$ at cold weather
- Presence of H_2O & CO_2 beneficial & SO_2 OK
- no N_2O formation
- No use of precious metal
  - Economical

[The above-described characteristics are all based on the inventor's published results]

ECH* vs. TWC** 比較

*ECH 適用於高效率汽油引擎以及柴油引擎
**因 TWC目前僅適用於汽油引擎, 本比較僅考慮汽油引擎

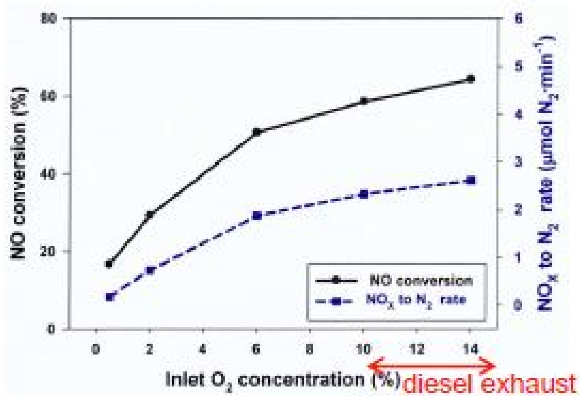
	ECH	TWC
富氧下de-NO_X能力	高 （所以ECH可使引擎在最省油狀態下操作）	無效 （所以TWC需在犧牲燃油效率狀態下操作）
對引擎燃油效率影響	引擎可控制在最佳燃油效率	引擎需控制在較低溫(較差燃油效率）
轉化器操作溫度	無 window 限制 (室溫到高溫皆可)	需高溫操作
貴重金屬	不需要	需要
de-NO_X 效率	高	較低
低溫起動 de-NO_X效率	高	幾乎無效
控制系統	僅需固定控制氣/燃比 (air/fuel ratio, A/F)~16.2	需作動態(dynamic)控制氣/燃比 在14.7上下，而約2/3時間需在14.7之下(還原態做NO_X還原）

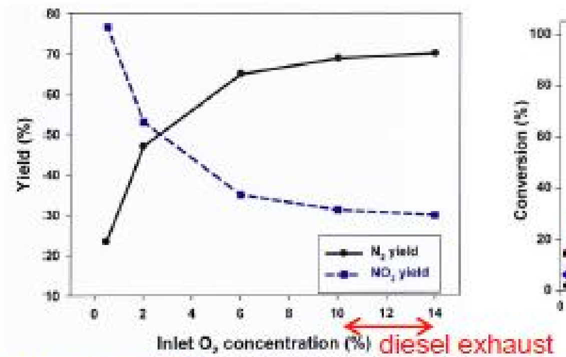
ECH vs. SCR*** 比較

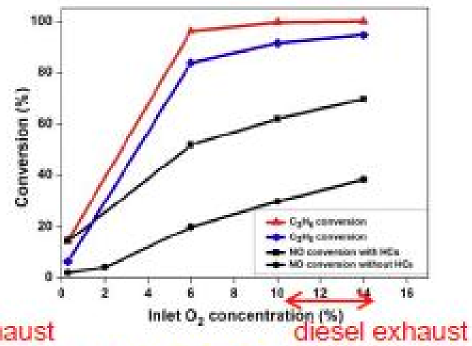
***因 SCR目前僅適用於柴油引擎, 本比較僅考慮柴油引擎

	ECH	SCR
還原劑外加	不需要	需要(尿素或氨水)
還原劑外洩疑慮	無	氨氣外洩 (二次汙染)
操作溫度	無 window 限制 (室溫到高溫皆可)	需高溫操作
廢氣中氧濃度限制	2 % 以上 越高越好(故最適合柴油廢氣處理)	6 % 左右較佳
N_2O (溫室氣體)	不會產生	會產生
De-NO_X 效率	高	較低
EGR 需求	不需要	需要
控制系統	不需要	需要, 需作回饋控制而無法及時妥善控制
其他	1. 可完全移除EGR系統而增加燃油效率 2. Soot/HC/CO 降低甚至不產生, 無需DPF	依環保要求而需搭配DPF (diesel particulate filter)

ECH 的相關deNO$_X$效能



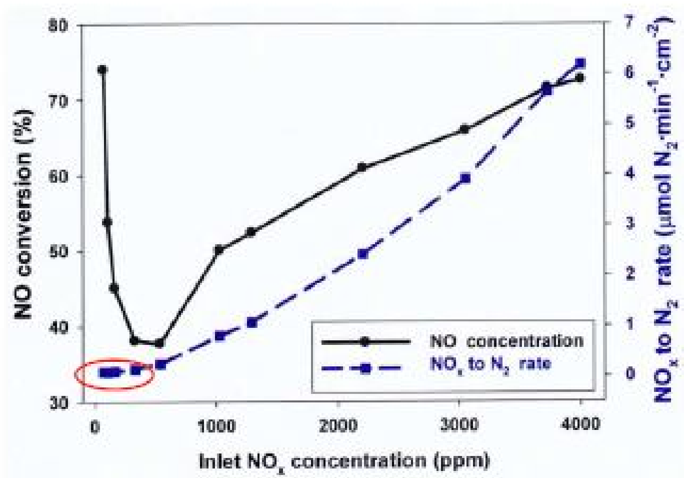




[T.J. Huang et al., *Appl. Catal. A* 445–446 (2012) 153]

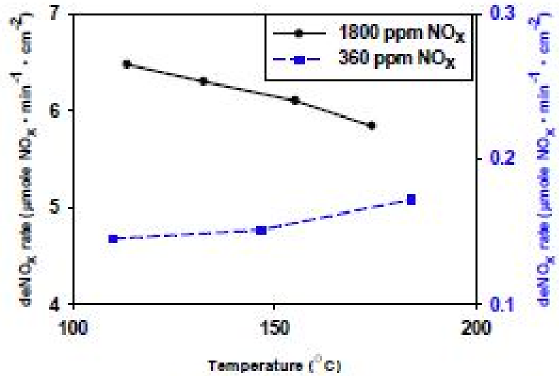
[T.J. Huang et al., *Appl. Catal. B* 110 (2011) 164]

Secondary air is beneficial



Very high NO$_X$ concentration preferred

[T.J. Huang et al., *Chem. Eng. J.* 203 (2012) 193]

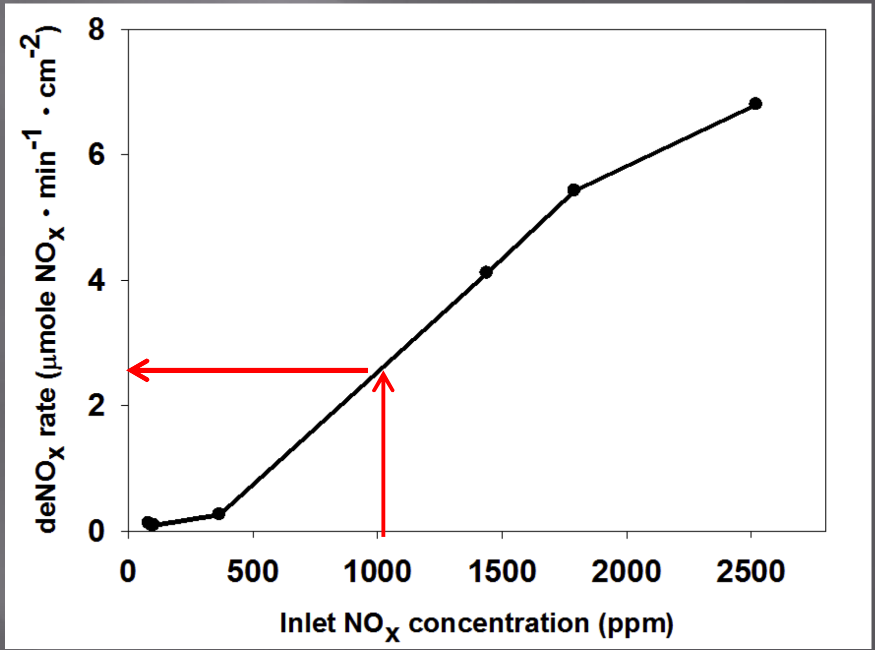


no treatment delay & no temperature window

These are typical characteristic curves for
promoted NO$_X$ Decomposition
for **lean** deNO$_X$ of combustion processes

ECH vs. SCR deNO$_X$ activity

	deNO$_X$ rate @ NO$_X$ 1000 ppm (μmole NO$_X \cdot$min$^{-1}\cdot$cm^{-2})	Condition
SCR	1.24 [O. Krocher, M. Elsener, ***Appl. Catal. B: Environ.*** 75 (2008) 215]	SCR-deNO$_X$ onboard of heavy-duty Diesel vehicles with commercial V_2O_5/WO_3–TiO_2 catalyst on standard metal substrates with a cell density (~honeycomb) of 400 cpsi, 400 °C.
ECH	2.5 [如下圖所示]	ECH-deNO$_x$ activities of treating Diesel-like gasoline engine exhausts. Cathode catalyst: $La_{0.58}Sr_{0.4}CoO_3$-$Ce_{0.9}Gd_{0.1}O_{1.95}$. The engine exhausts contain various NO$_x$, 15±1 % O_2 and 4% CO_2 at 135±17 °C; space velocity of 3.72±0.25 x10^5 h^{-1}.



ECH
緊密小巧而有大功能

- **ECH 所需的體積 相當於引擎的體積**
  - **2120 cm^3 @ 400 cpsi (30 cm^2 treating area/cm^3)**

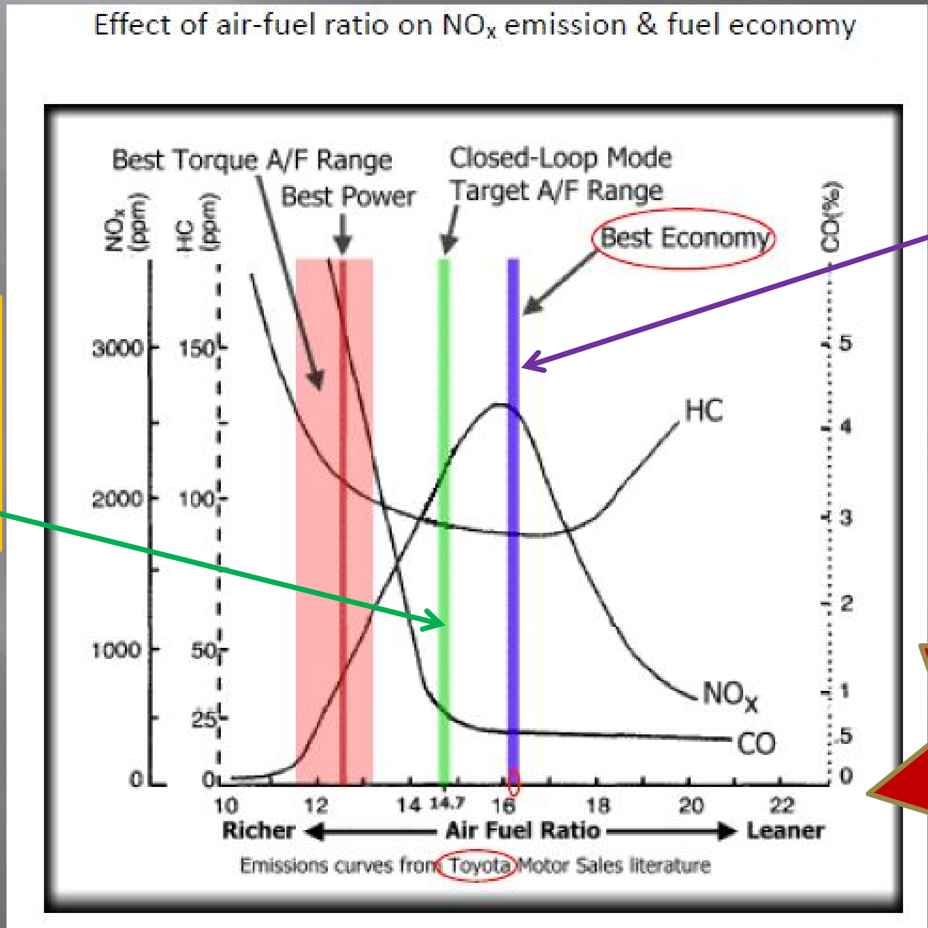
- 計算基準
  - **2000 cc 汽油車在富氧燃燒狀況下**
  - **NO_X 濃度約 4000 ppm**

[L. Guzzella, C.H. Onder, Introduction to modeling and control of internal combustion engine systems, Springer-Verlag, Berlin (2010)]

  - **95% NO_X 去除率**
  - **相當於 deNO_X 平均速率 2.54 ·10^5 μmole NO_X min^{-1}**
  - **ECH 平均 deNO_X 速率 4 μmole NO_X min^{-1} cm^{-2}**

兼俱環保及燃油效能的最佳方案
汽油車的應用

符合最新
EURO 6環保
法規



舊技術
- 氣燃比控制 **14.7**
  → 燃油效率較低
- **TWC** 轉化器

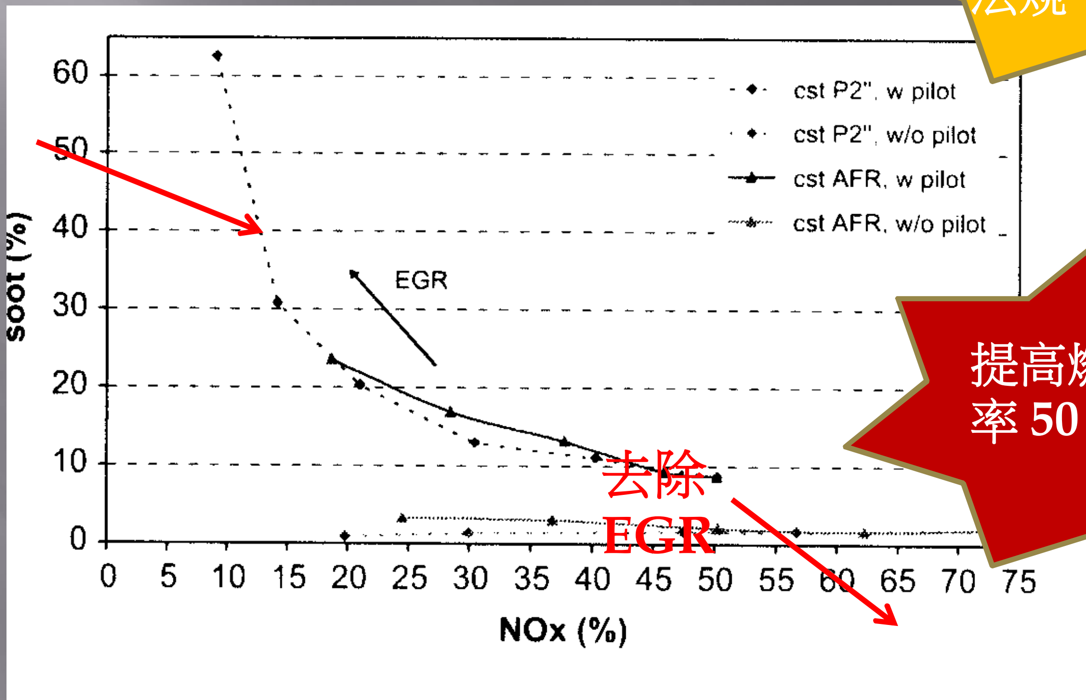
新技術
- 氣/燃比控制~**16.2**
  → 燃油效率最佳
- **ECH**轉化器
  因為 **ECH**可在富氧環境除去高濃度NO_X

提高燃油效率 **50 %**

兼俱環保及燃油效能的最佳方案
柴油車的應用

符合最新
EURO 6環保
法規

舊技術
- EGR → 加裝DPF
- SCR de-NO_X



提高燃油效
率 50 %

柴油引擎 NO_X－soot 特性曲線*

* NO_X-soot trade-off during exhaust gas recirculation (EGR) of diesel engine
[Energy 33 (2008) 22]

新技術
- 無 EGR → 不用加裝DPF
- ECH de-NO_X

因為ECH可在富氧環境除去高濃度NO_X

Mechanisms of *emf-promoted decomposition*

NO_x: NO & NO_2

$NO \leftrightarrows N + O$ (previously needing removal by reductant NH_3,CO,HCs)

$\downarrow \quad \downarrow$ SCR↑,TWC↑

$N_2 \quad O_2$ (continuously promoted oxygen desorption--PND)

$\uparrow$

$NO_2 \leftrightarrows NO + O$

$O_2 \leftrightarrows 2O$

SO_x: SO_2 & SO_3

$SO_2 \rightarrow 1/8S_8 + 2O \rightarrow O_2$ (promoted oxygen desorption)

$SO_3 \leftrightarrows SO_2 + O$

promoted NO_x decomposition--PND vs. **LNT**NSR & **SCR**

promoted SO_x decomposition--PSD

continuously promoted oxygen desorption by the presence of a voltage (an electromotive force, ***emf***)

Publications supporting lean deNOx by promoted NO_X decomposition (PND)

underlined is the inventor of the ECH.

- Ta-Jen Huang, C.L. Chou, ***Electrochem. Comm.***, 11 (2009) 477–480.
- Ta-Jen Huang, C.L. Chou, ***J. Power Sources***, 193 (2009) 580–584.
- Ta-Jen Huang, C.L. Chou, ***J. Electrochemical Society***, 157 (2010) P28–P34.
- Ta-Jen Huang, C.L. Chou, ***Chem. Eng. J.***, 160 (2010) 79–84.
- Ta-Jen Huang, C.L. Chou, ***Chem. Eng. J.***, 162 (2010) 515–520.
- Ta-Jen Huang, I.C. Hsiao, ***Chem. Eng. J.***, 165 (2010) 234–239.

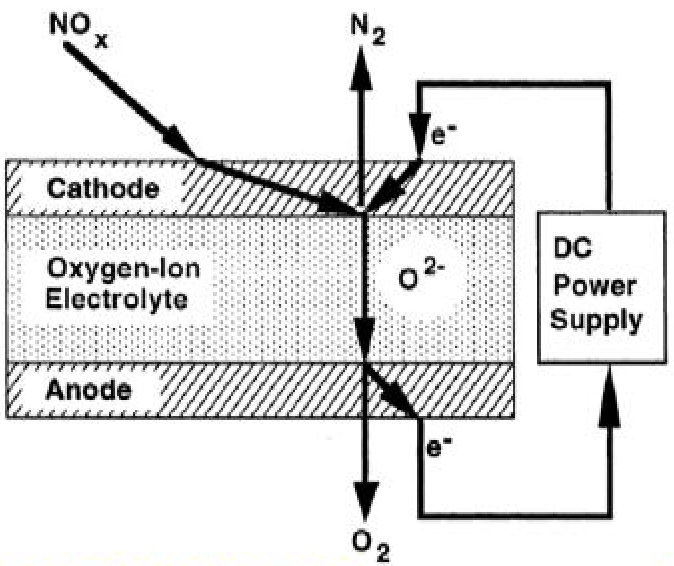
Power generation with NO_x substituting O_2
-- NO_x decomposition in rich oxygen
-- promoted by both voltage & oxygen-ion migration

- Ta-Jen Huang, C.Y. Wu, Y.H. Lin, ***Environmental Science Technology***, 45 (2011) 5683–5688.
- Ta-Jen Huang, C.Y. Wu and C.C. Wu, ***Chem. Eng. J.***, 168 (2011) 672–677.
- Ta-Jen Huang, C.Y. Wu, C.C. Wu, ***Electrochem. Comm.***, 13 (2011) 755–758.
- Ta-Jen Huang, C.Y. Wu, C.C. Wu, ***Chem. Eng. J.***, 172 (2011) 665–670.

NO_x decomposition at (promoted by) open-circuit voltage (electromotive force, *emf*)

- Ta-Jen Huang, C.Y. Wu, S.H. Hsu, C.C. Wu, ***Energy Environmental Science***, 4 (2011) 4061–4067.
- Ta-Jen Huang, C.H. Wang, ***Chem. Eng. J.***, 173 (2011) 530–535.
- Ta-Jen Huang, C.Y. Wu, S.H. Hsu, C.C. Wu, ***Appl. Catal. B: Environmental***, 110 (2011) 164–170.
- Ta-Jen Huang, C.Y. Wu, ***Chem. Eng. J.***, 178 (2011) 225–231.
- Ta-Jen Huang, C.H. Wang, ***J. Electrochemical Society***, 158 (2011) B1515–B1522.
- Ta-Jen Huang, S.H. Hsu, C.Y. Wu, ***Environmental Science Technology***, 46 (2012) 2324–2329.
- Ta-Jen Huang, C.Y. Wu, D.Y. Chiang, C.C. Yu, ***Chem. Eng. J.***, 203 (2012) 193–200.
- Ta-Jen Huang, C.Y. Wu, D.Y. Chiang, C.C. Yu, ***Appl. Catal. A: Gen.***, 445–446 (2012) 153–158.
- Ta-Jen Huang, C.Y. Wu, D.Y. Chiang, ***J. Ind. Eng. Chem.***, 19 (2013) 1024–1030.

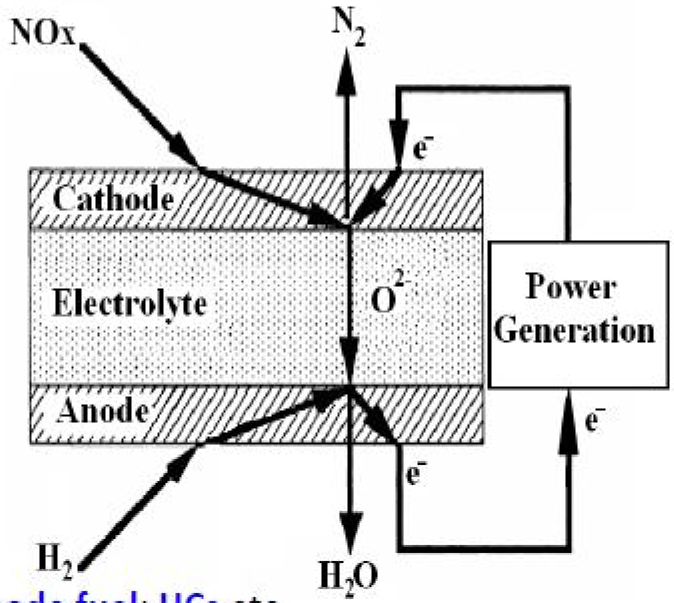
emf ↔ open-circuit voltage (OCV) of fuel cell



no anode fuel needed

with **applied voltage**

— **oxygen pumping**



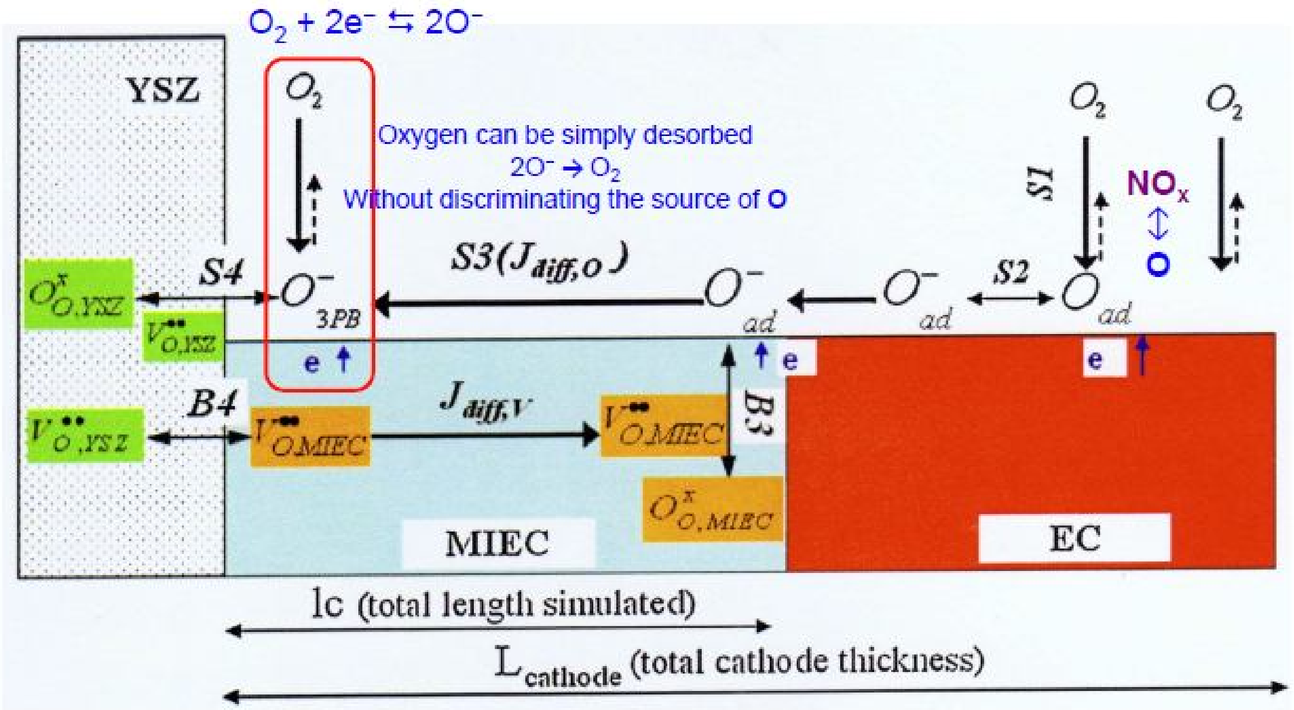
Anode fuel: HCs etc.

with **power generation**

— **solid oxide fuel cell** (SOFC)

-- continuous presence of an OCV for power generation

Principle for *emf-promoted decomposition of NO → $N_2 + O_2$*



Schematic description of bi-pathway dominated **oxygen reduction** on **SOFC** cathode

[M. Gong, R.S. Gemmen, X. Liu, *J. Power Sources* 201 (2012) 204]

Lean deNOx by emf-promoted decomposition of NO_x

$NO \rightarrow N + O$ $\Delta H_{298} = -21.6$ Kcal/mole (exothermic)

$NO_2 \rightarrow N + O_2$ $\Delta H_{298} = -8$ Kcal/mole

at high enough NO concentration

$2NO + [\,]\cdot[\,] \rightarrow N\!-\![O]\cdot[O]\!-\!N$

$N\!-\![O]\cdot[O]\!-\!N \rightarrow N_2 + [O]\cdot[O]$

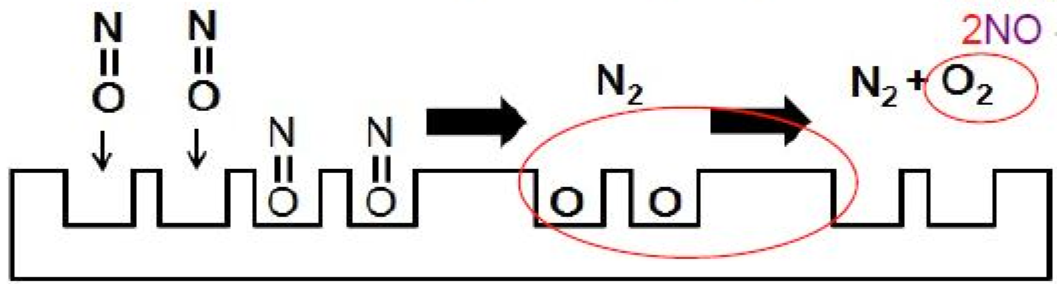
$[O]\cdot[O] \rightarrow O_2 + [\,]\cdot[\,]$

2nd order

$r_{N2} = k\,[NO]^2$

Higher NO concentration is highly preferred (according to kinetic law)

$2NO \rightarrow N_2 + O_2$



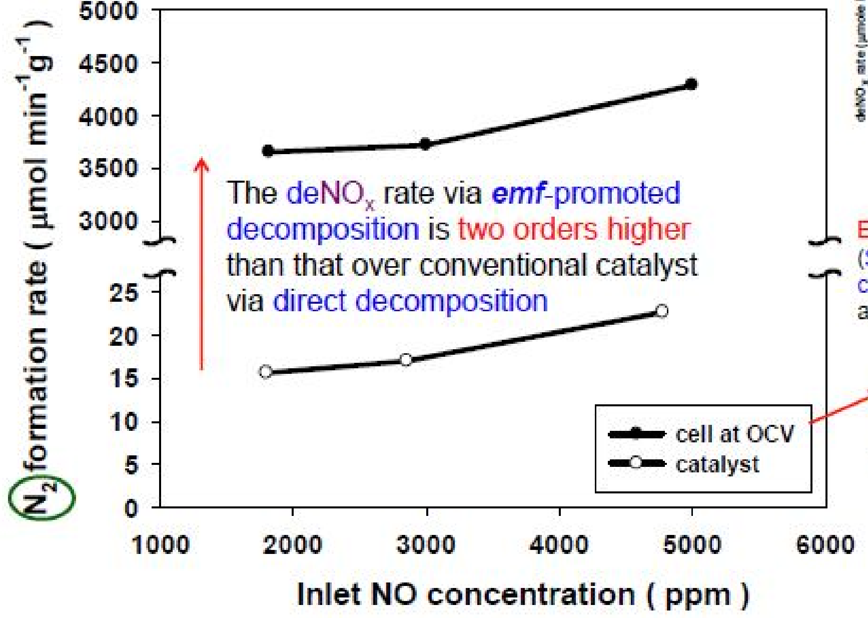
The presence of a voltage weakens the chemisorptive bond strength of the O species.

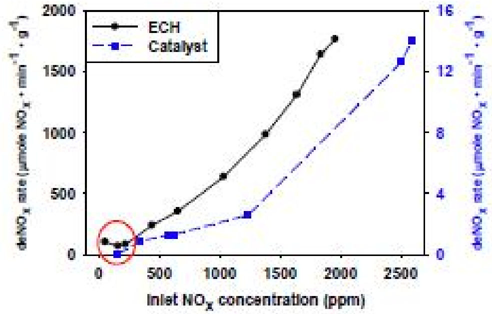
[C.G. Vayenas, S. Bebelis, *Catal. Today* 51 (1999) 581]

→ **facile desorption of oxygen**

for *emf*-promoted decomposition of NO_x

Principle and proof for *emf-promoted decomposition of NO → $N_2 + O_2$*





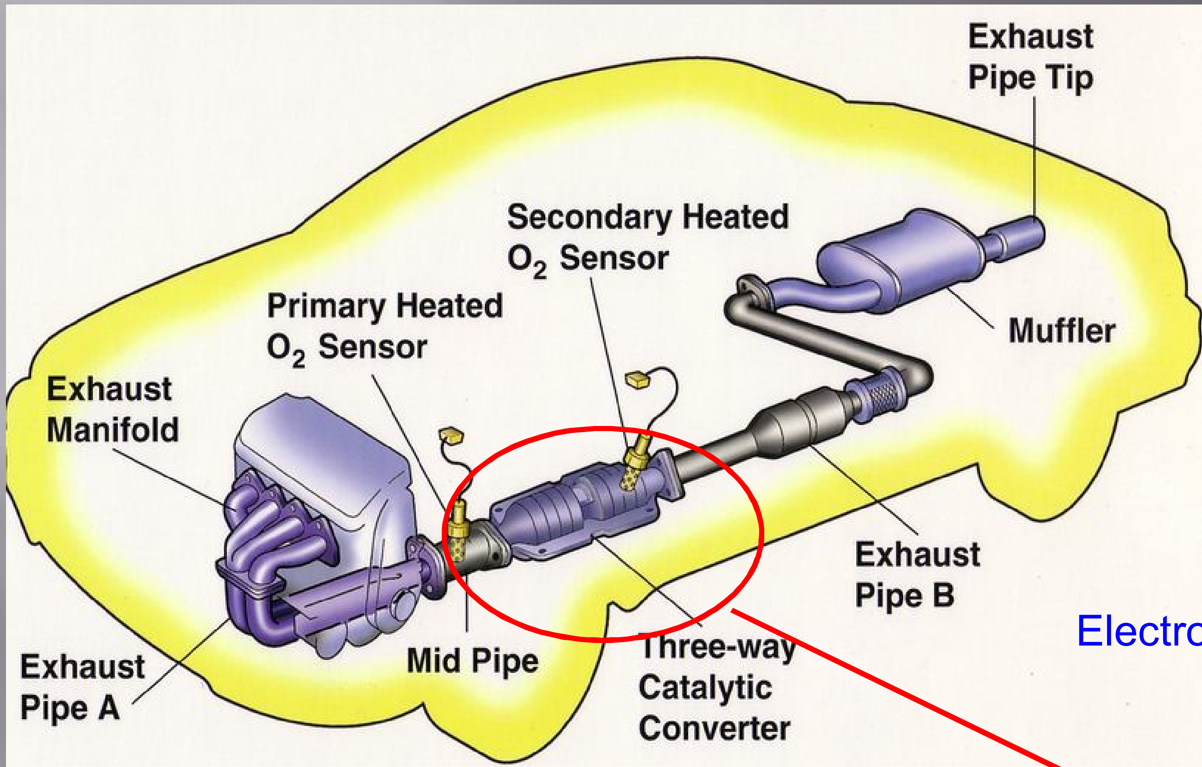
Electrochemical cell can be solid oxide fuel cell (SOFC) --1st stage of this tech, electrochemical-catalytic cell (ECC), electro-catalytic tube (ECT) and EDC in electro-catalytic honeycomb (ECH).

OCV: open-circuit voltage
(solid oxide fuel cell operation without consuming anode fuel, *i.e.*, reductant)
~ electromotive force (*emf*)

Electrochemical cell : LSC –GDC cathode
Catalyst : LSC –GDC
($La_{0.6}Sr_{0.4}CoO_3$ –$Ce_{0.9}Gd_{0.1}O_{1.95}$)
14% O_2, 10% H_2O, 10% CO_2; 600°C

Over the catalyst in a conventional reactor, the formed N species from direct NO decomposition can be easily associated to form N_2; however, the formed O species is strongly adsorbed and facile desorption of the O species as O_2 into the gas phase is very important.
[Y. Teraoka et al., *J. Chem. Soc. Faraday Trans.* 94 (1998) 1887]

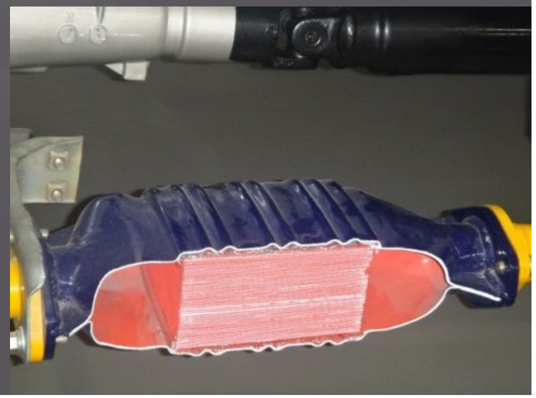
汽油車新舊車改裝



(TWC)

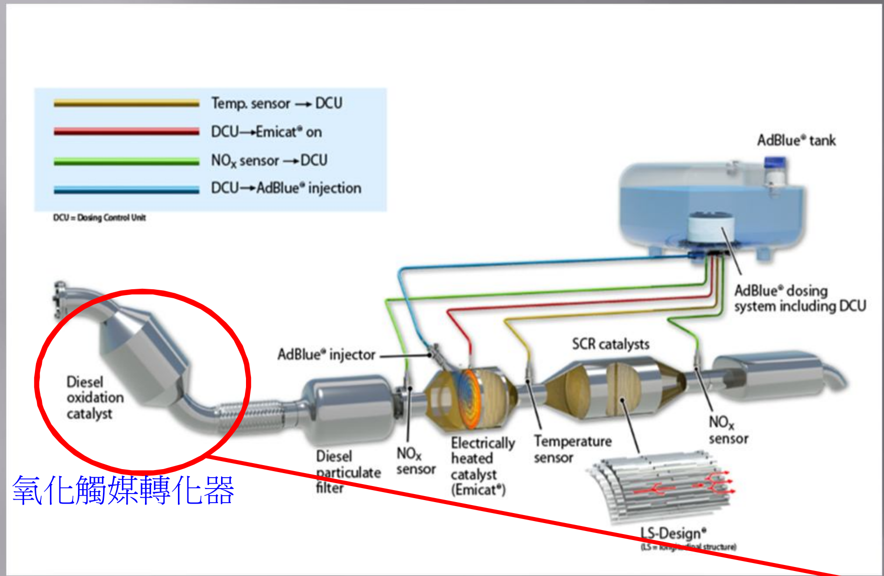
TWC換成ECH
A/F調整為16.2

Electro-Catalytic Honeycomb (ECH)



柴油車舊車改裝

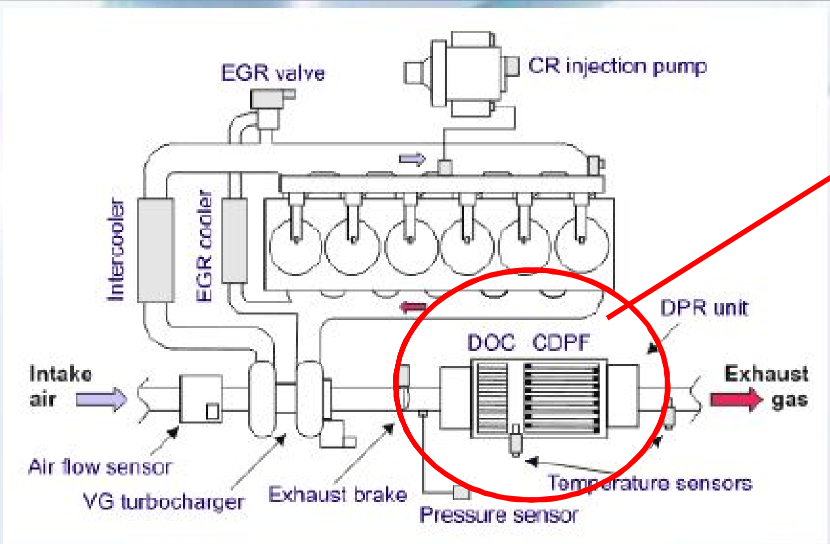
CASE 1



氧化觸媒轉化器
換成ECH
EGR系統關閉
SCR系統停用

Electro-Catalytic Honeycomb (ECH)

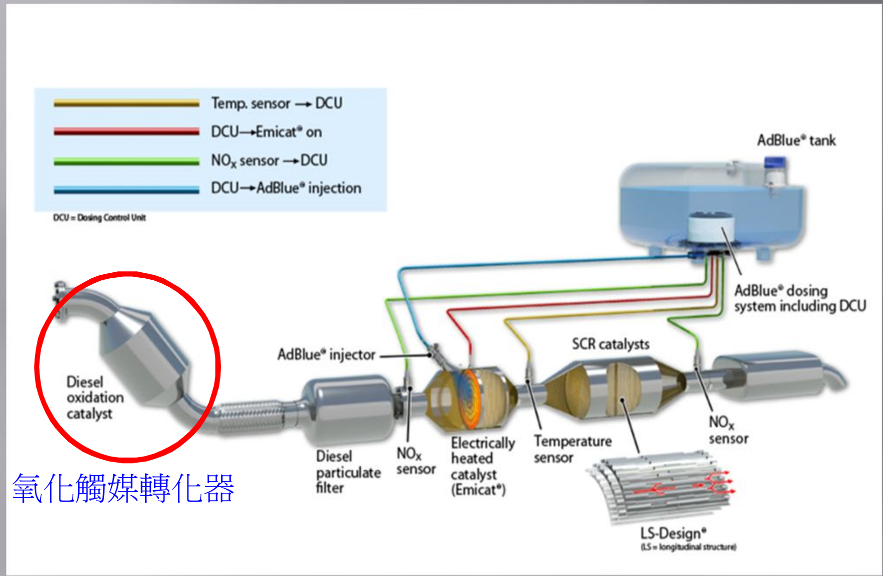
CASE 2



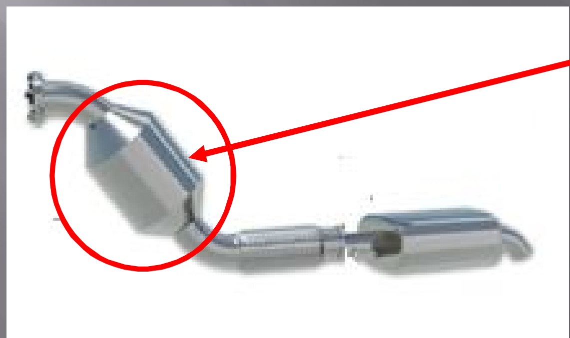
引擎與被動再生濾煙器關係圖

氧化觸媒轉化器(DOC)/柴油濾煙器(DPF)換成ECH
EGR系統關閉
SCR系統停用

柴油車新車裝置



氧化觸媒轉化器
換成ECH
EGR及其他廢氣
處理系統移除



Electro-Catalytic Honeycomb (ECH)