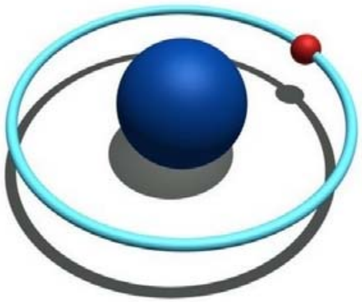
다성분계 3차원 나노구조체를 이용한 고성능 수소 센서 기술(1%농도 2초대 검출)

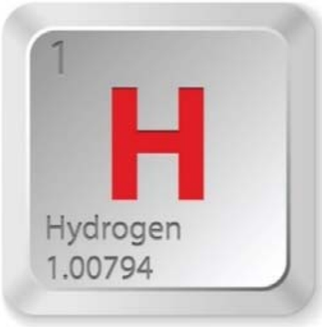
한국과학기술원 (KAIST)
생명화학공학과 & 나노융합연구소

정 희 태 교수

[INTRODUCTION – 수소]

- **Hydrogen (H_2, 수소)**





가장 강력한 대체에너지 (석유의 3배에 해당하는 에너지 밀도)

Energy densities of common energy storage materials

Storage material	Energy type	Specific energy (MJ/kg)
Tritium	Nuclear decay	583,529
Hydrogen (compressed at 700 bar)	Chemical	142
Methane or Liquefied natural gas(compressed)	Chemical	55.5
Diesel	Chemical	48

From Wikipedia

- 매우 낮은 밀도 (0.0899 kg/m^3)
- 높은 확산 계수 (0.61 cm^2/s)
- 낮은 발화 에너지 (0.017 mJ)
- 매우 높은 연소열 (142 kJ/g H_2)
- 넓은 발화 농도 범위 (4-75%)

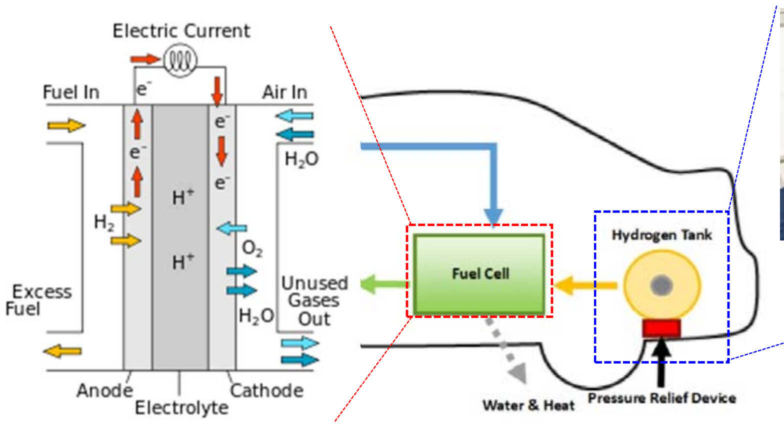
안전한 저장 및 이동

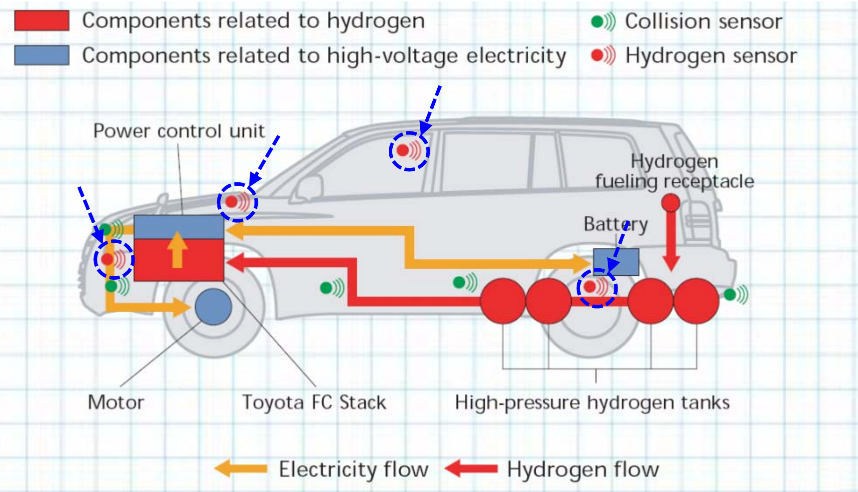
빠른 누출 감지

수소 에너지 이용의 필수요건

[INTRODUCTION – 수소 센싱 기술의 응용]

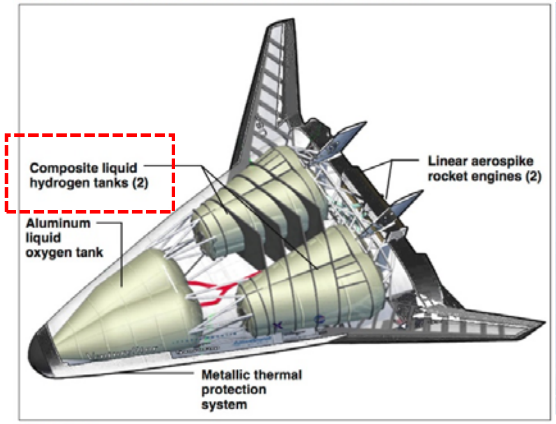
- **연료전지 하이브리드 자동차**: Fuel-Cell-Hybrid Vehicle (FCHV)



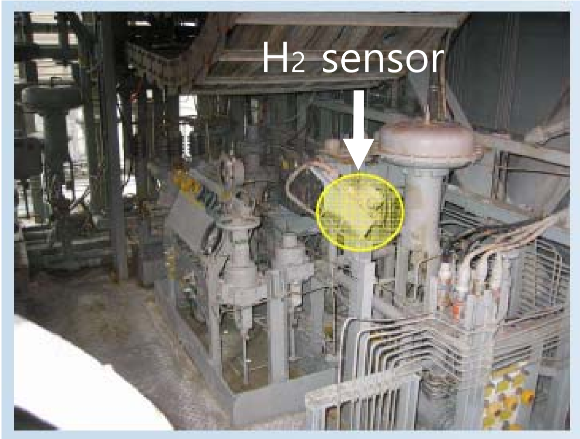


- **우주 기술 (Space Technology)**

Figure 3: Cutaway Interior Illustration of the Planned X-33 Vehicle



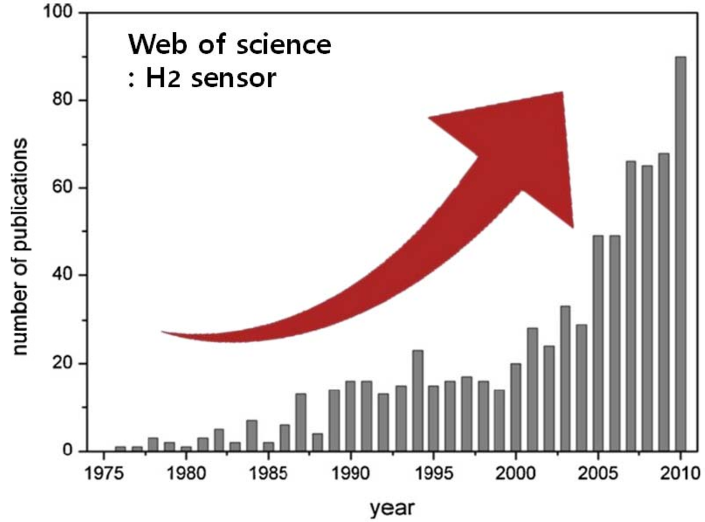
Source: NASA.



[INTRODUCTION – 수소 센서 Market]

- 가스 센서 글로벌 마켓 규모: 1,297.6 Million $ by 2023 / CAGR 6.83%
  수소 글로벌 마켓 규모: 183.34 Billion $ by 2023 / CAGR 6%

급증하는 연구 추세



[INTRODUCTION – 기존의 수소 센싱 기술]

- **Electrochemical Sensors**

:Amperometric, potentiometric [low T and high T]; solid/liquid electrolyte

- **Pd-film and Pd-alloy films**

: Electronic -resistor, capacitor, transistor
: Thermoelectric
: Optical evanescent wave
: Mechanical [SAW, cantilever]

- **Metal Oxide Sensors (MOX sensors)**

: Heated metal oxides

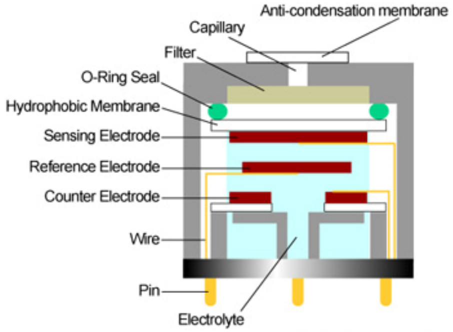
- **Pellistor-type combustible gas sensors**

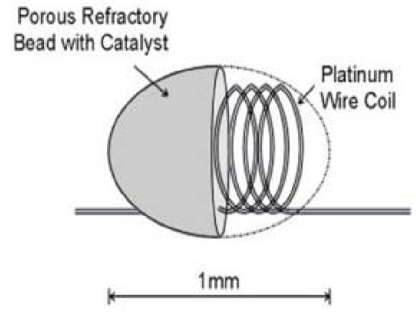
: Hot Pt or Pd catalyst with Pt resistance thermometer

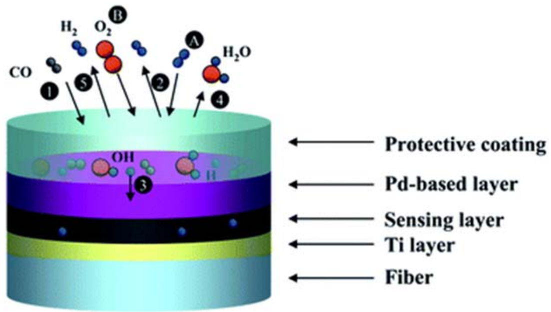
- **Thermal conductivity**

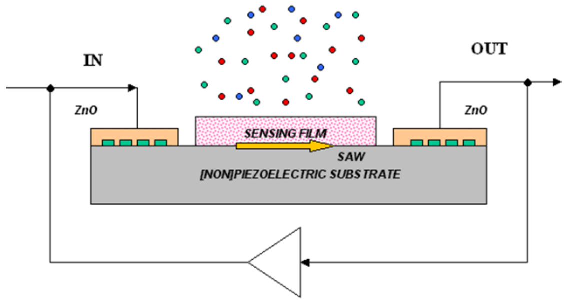
- **Optical Devices**

: colorimetric and indicator dyes
: Evanescent wave – with film of Pd or other material









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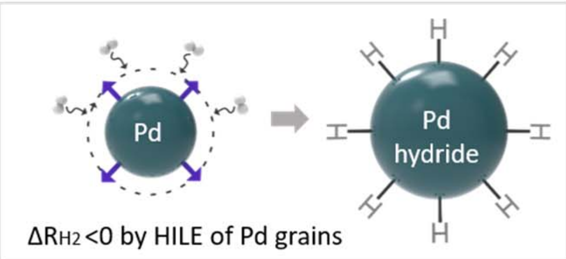
[INTRODUCTION – 수소 센싱의 원리]

▪ Palladium (Pd, 팔라듐): 가장 강력한 수소 센싱 재료

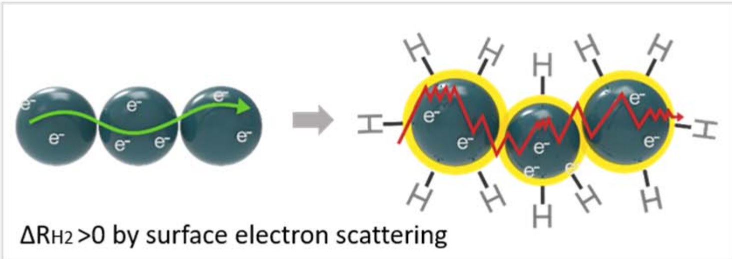
- Pd called "metal sponge" to H_2 (can absorb 900 times of its volume)
- H_2 sensing mechanism : α to β transition with Pd-H

$$\mathrm{Pd-O} + \frac{3}{2}\mathrm{H_2(ads)} \rightarrow \boxed{\mathrm{Pd-H}} + \mathrm{H_2O(ads)}$$

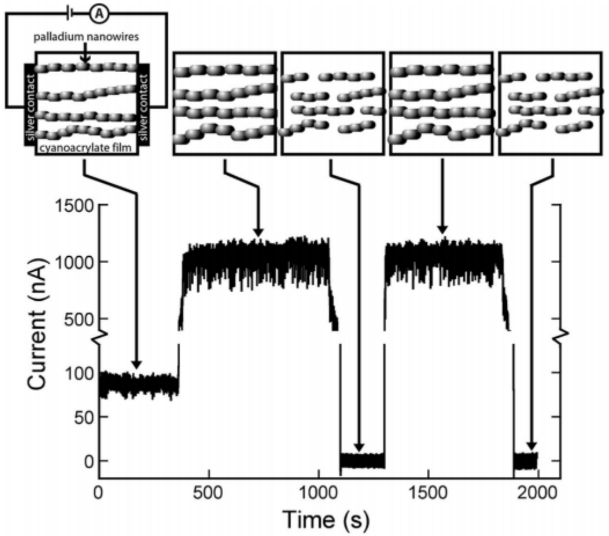
$$\mathrm{H_2O(ads)} \rightarrow \mathrm{H_2O(g)}$$



Lattice constant 3% increase



Resistivity increases 2-times



R. M. Penner, et al. *Science* **2001**

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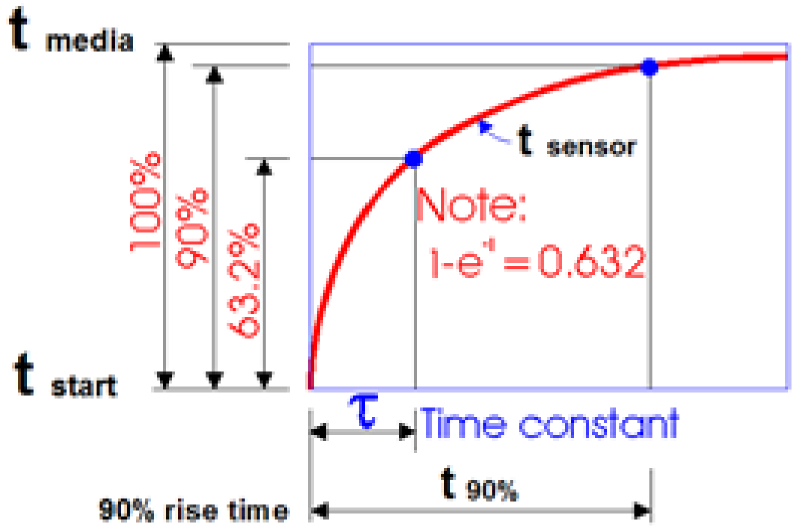
[INTRODUCTION – 수소 센서의 요건]

▪ 미국 에너지부 (U.S. department of energy (DOE)) 요구 사항

Parameter	Target
Sensitivity	25% (1% of H_2)
Range	0.1 – 4 %
Power	<100 mW
Lifetime	5 years
Response time	< 1 min at 1% < 1 sec at 4 %
Recovery time	60 sec



빠른 감지를 통한 누출 차단 및 폭발 전 대피를 위해 반응 속도를 가장 엄격하고 중요시 함

→ 하지만 여전히 60초 이하의 요구 조건을 만족하는 센싱 기술을 많지 않음

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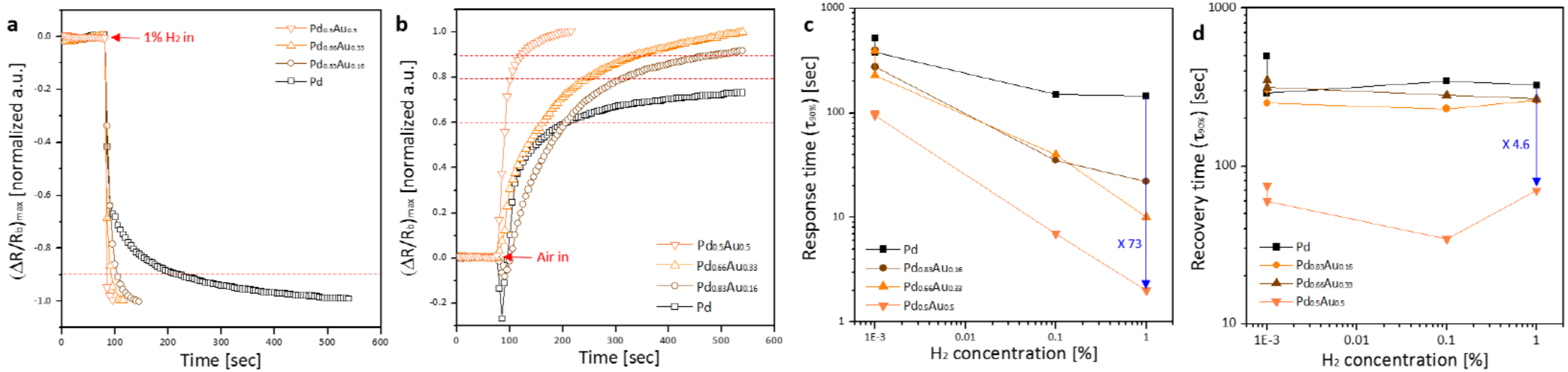
[본 기술의 특징 1. 매우 빠른 반응 속도]

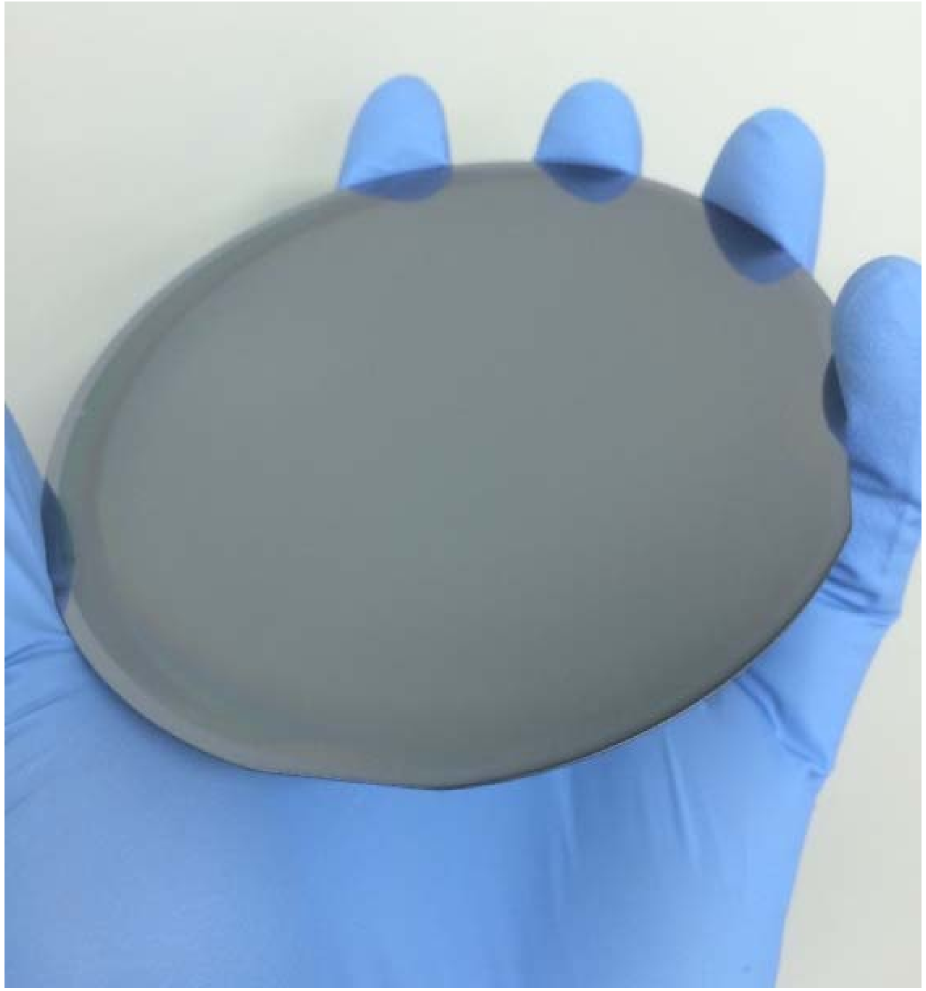
- 기존 Pd 기반 센서 대비 최대 80배 증가된 반응 속도

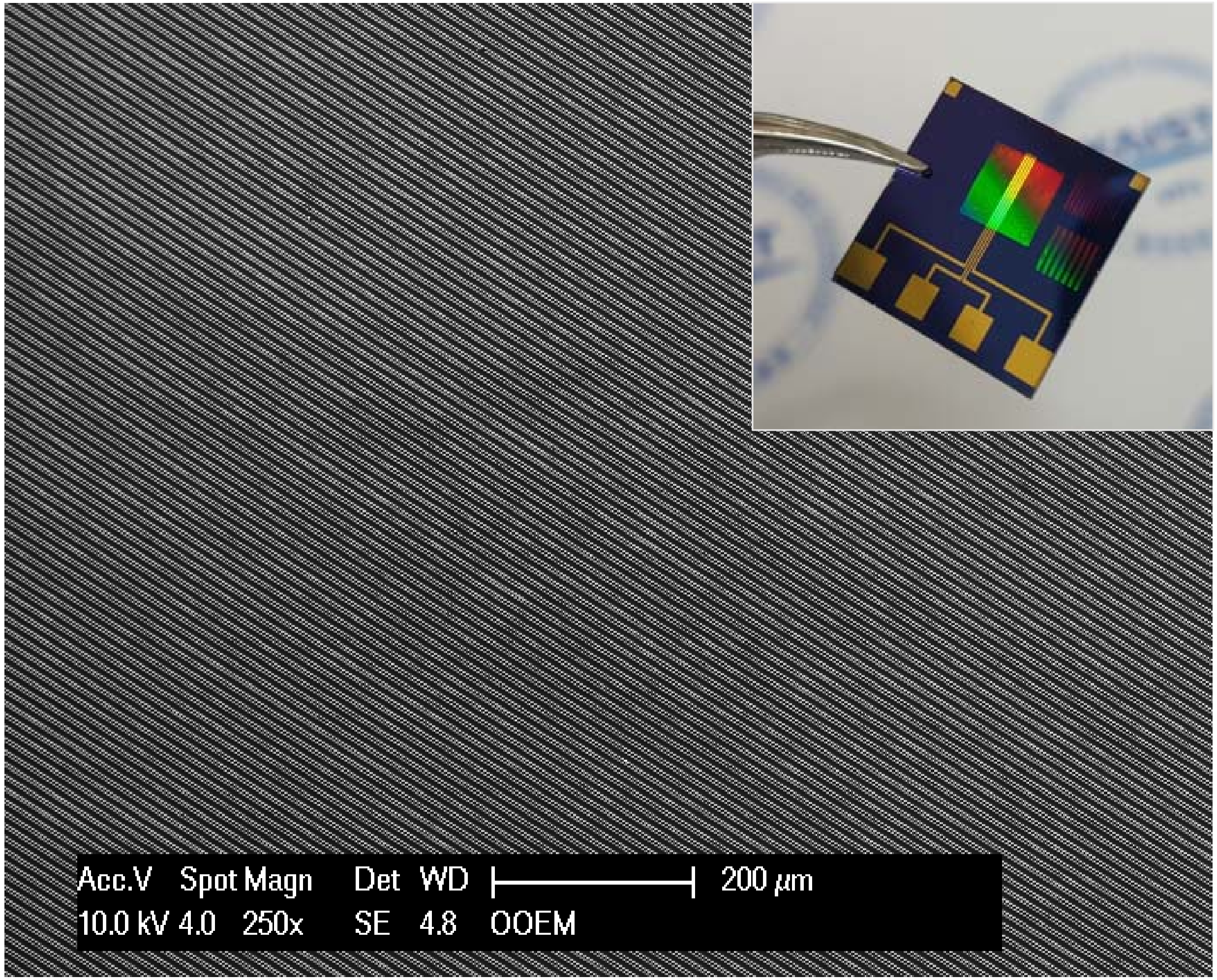


- **현재까지 보고된 팔라듐을 이용한 센서 중 가장 빠른 반응 속도를 보고함 (1% 수소에 2초 대의 반응 속도)**

materials[a]	response at 0.1% $[H_2]$	τ_{resp}/τ_{rec}[b] at 0.1% $[H_2]$	detection limit $([H_2])$
Pd/Ni film (t = 50 nm)	nr	120 s/20 s	nr
Pd NW (d = 50–80 nm)	~1%	nr	1000 ppm
single Pd NW (25 (h) × 85 nm (w))	3%	400 s/1000 s	100 ppm
single Pd@Pt NW (40 (h) × 100 nm (w))	nr	250 s/15 s	0.2%
Pd nanotube	2%	80 s/nr	500 ppm
Pd nanotube	1000%	190 s/nr	100 ppm
Pd NWs@ZIF-8_2 h	0.3%	13 s/6 s	1000 ppm
Pd NWs@ZIF-8_4 h	0.7%	30 s/8 s	600 ppm

[본 기술의 특징 2. 대면적 제조 가능 및 IC Compatibility]





기존 센서 기술들의 상업화에 있어 가장 큰 두가지 걸림돌

[본 기술의 특징 3. Scale-up 가능성 및 경제성]

- 국가나노종합기술원에서 차세대 나노기법으로 인정하여 **Scale-up 장비 설비**

대형 Ar milling 장비

→ 8인치 웨이퍼 스케일
대면적 공정 구축

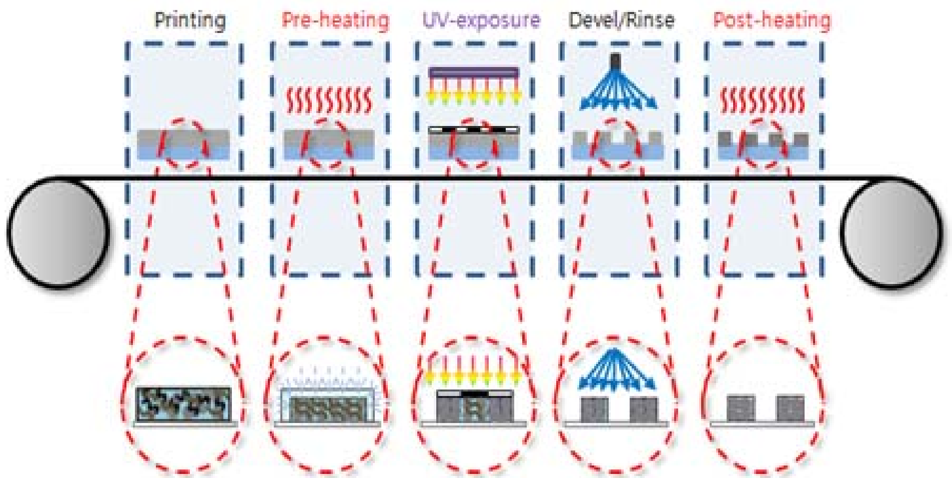
→ 중소기업 연계를 통한
외부 기술 지원

→ 공동 연구를 통한
연구 영역 확대

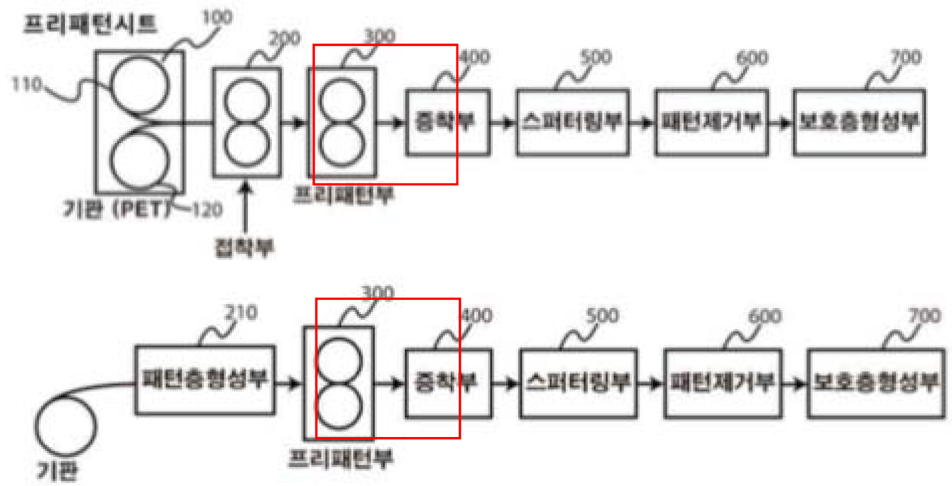
[본 기술의 특징 3. Scale-up 가능성 및 경제성]

▪ 경제성/생산성

- **기존 리소그래피 공정을 활용**할 수 있으며, **고가의 장비 없이** 구현 가능
- 롤투롤 공정으로 **연속 공정 가능**



기존 포토리소그래피 공정



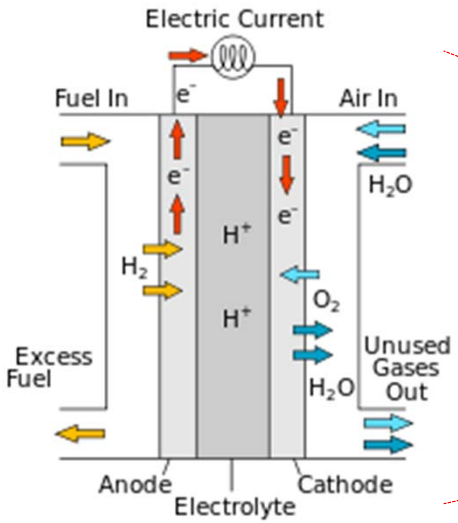
스퍼터링부 추가로 공정 진행 가능

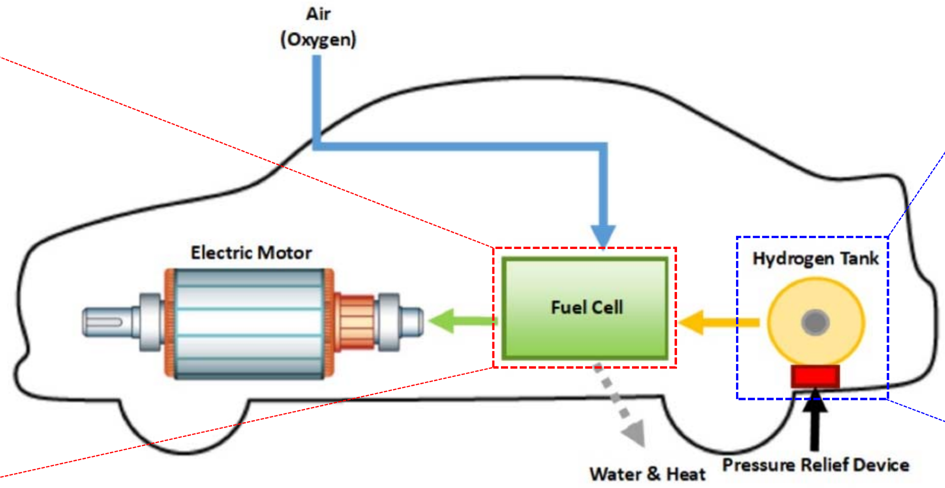
감사합니다

기술이전 문의: mjseo@kaist.ac.kr

[APPENDIX I – 수소 센싱 기술의 응용분야 (1)]

- **연료전지 하이브리드 자동차**: Fuel-Cell-Hybrid Vehicle (FCHV)





- Honda™ FCHV의 경우
  : Tank Pressure 4.1 kg Hydrogen at 5000 psi

→ 142 kJ/g H2 X 4.1 kg = **582200 kJ (0.2톤 TNT)**

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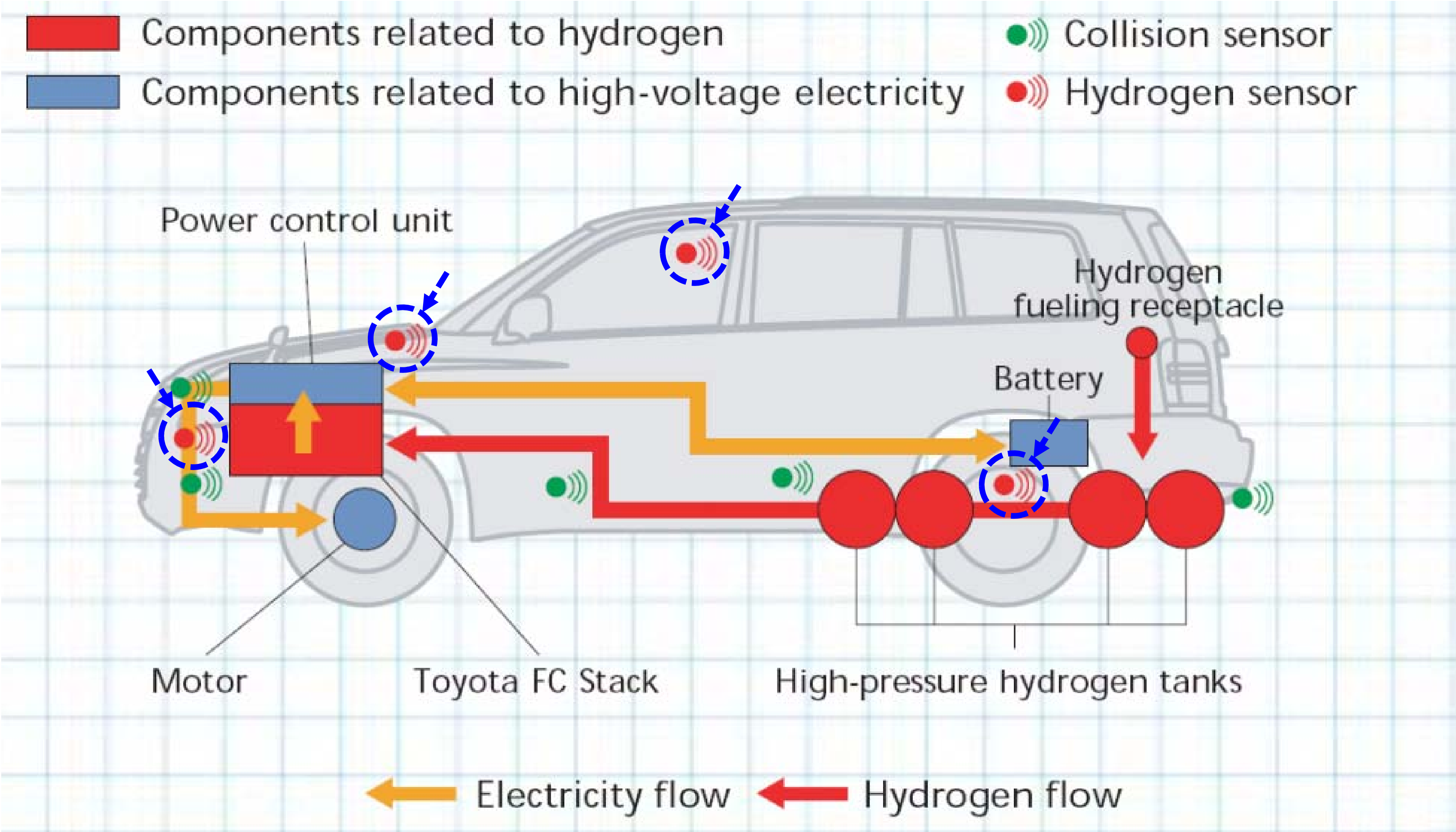
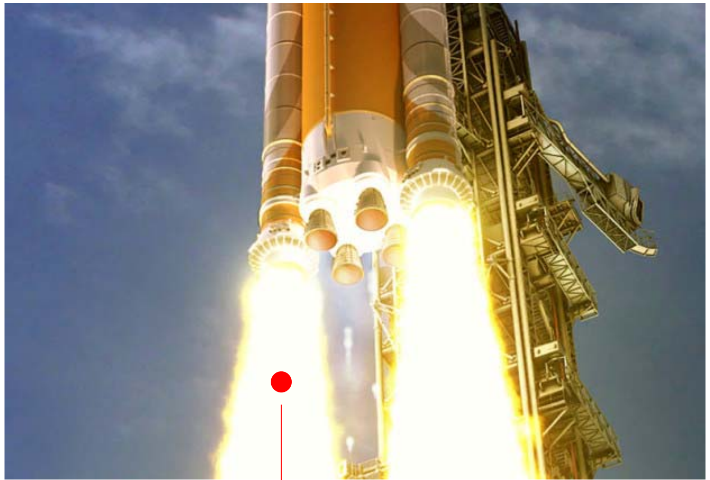
[APPENDIX II – 수소 센싱 기술의 응용분야 (1)]



[APPENDIX III – 수소 센싱 기술의 응용분야 (2)]

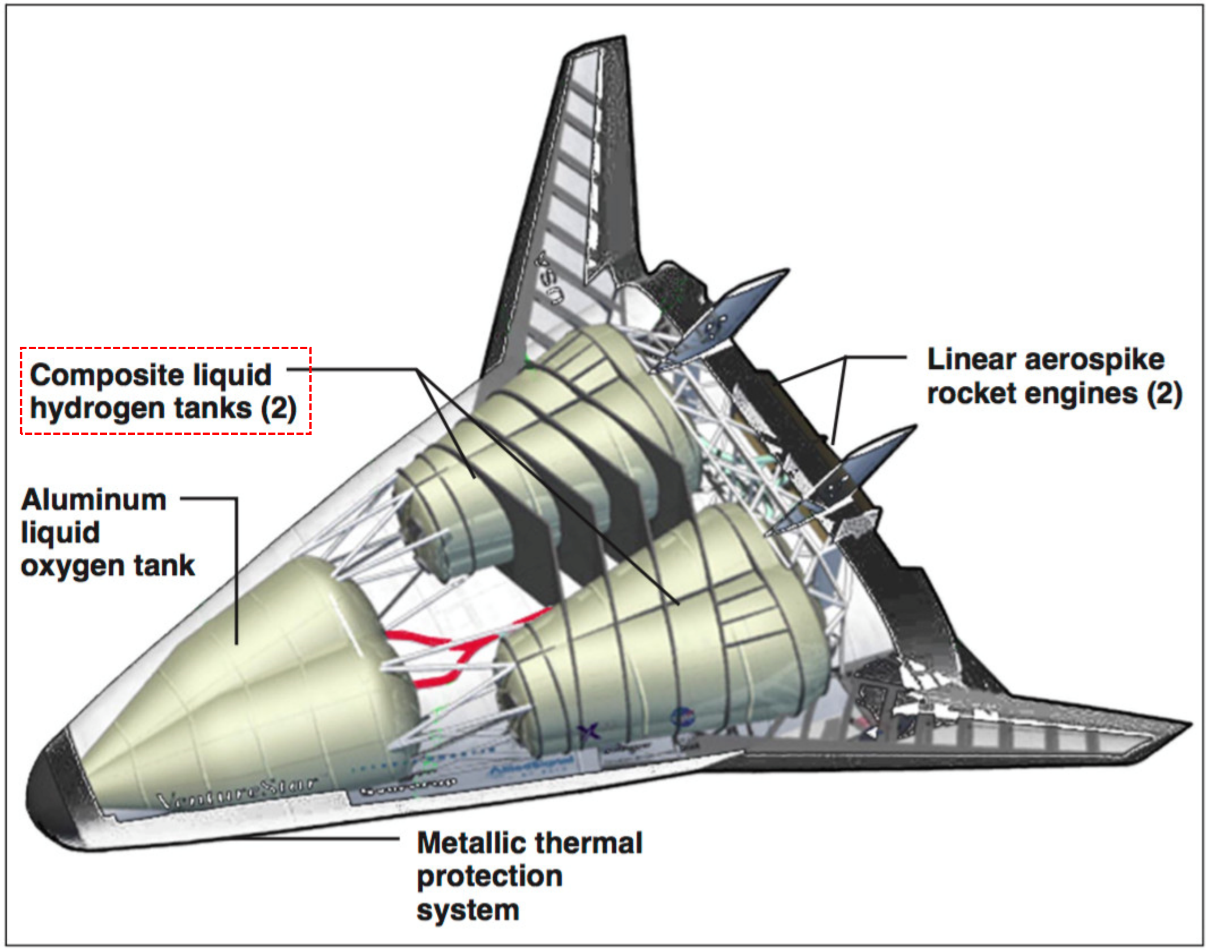
- 우주 기술 (Space Technology)



Exothermic Reactions

$2H_2 + O_2 = 2H_2O + Energy$

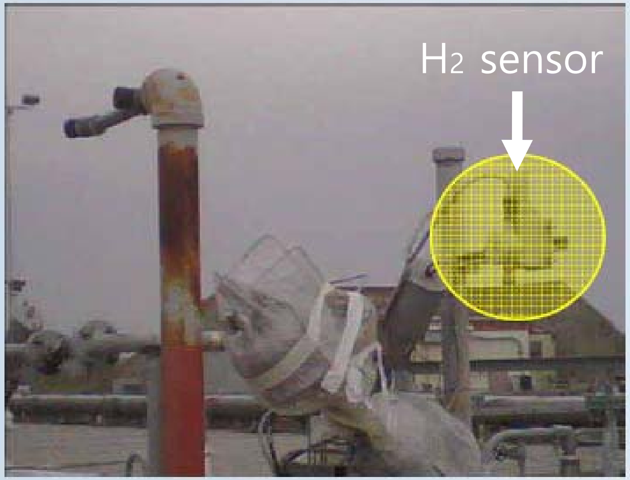
Figure 3: Cutaway Interior Illustration of the Planned X-33 Vehicle

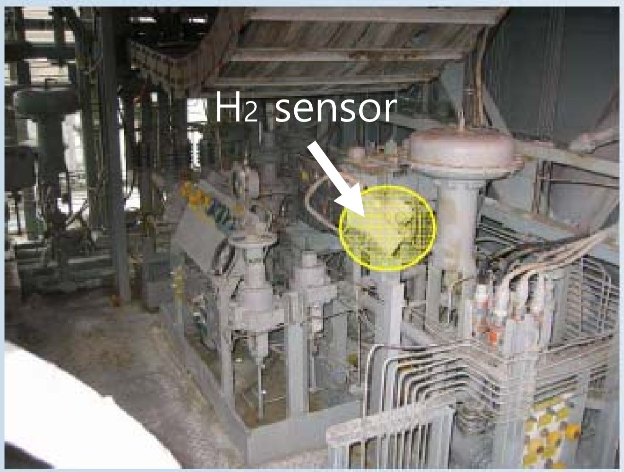


Source: NASA.

[APPENDIX IV – 수소 센싱 기술의 응용분야 (2)]

Data from Element One, Inc.





- **NASA/Kennedy Space Center**

- 액체 수소 저장 및 공급 라인

- 800,000 Gallon liquid H_2 tank
- Numerous Electronic Sensors for H_2 leakage detection

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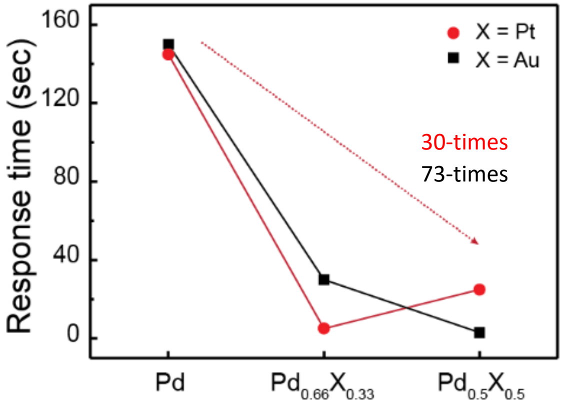
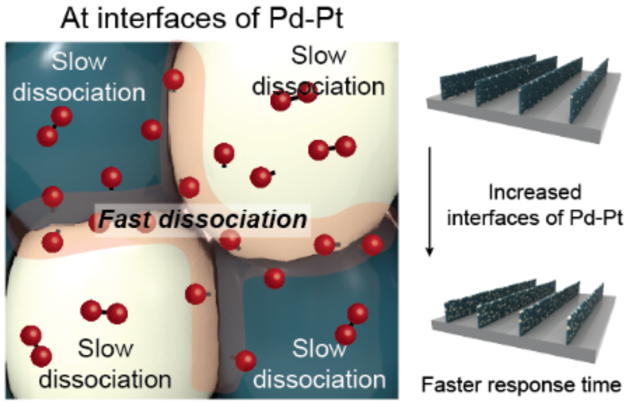
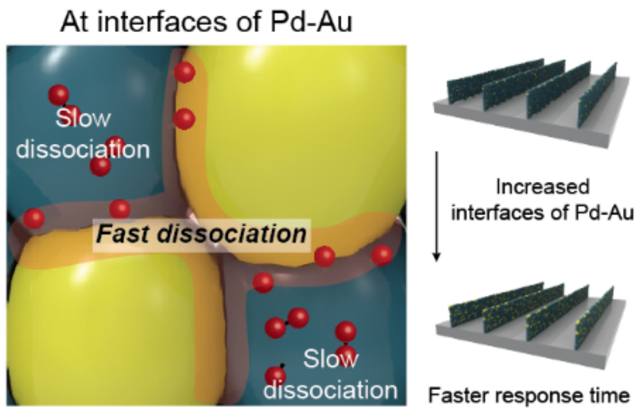
[APPENDIX VIII – Faster Response Behavior]

- **Decrease of response time**



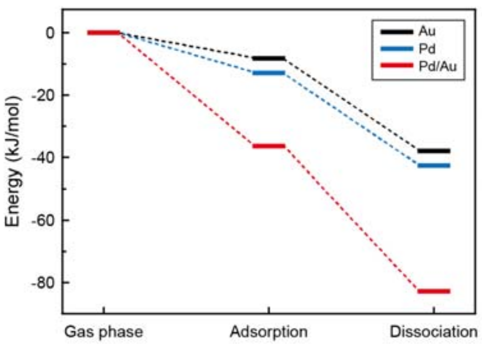




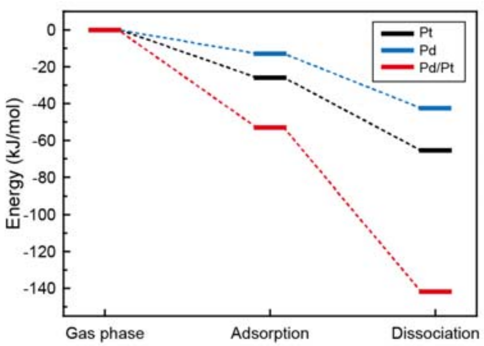
J. Phys. Chem. C **2011** *J. Phys. Chem. C* **2013**

- **Adsorption/Dissociation energy calculation (DFT)**

[Au/Pd case]



[Pt/Pd case]



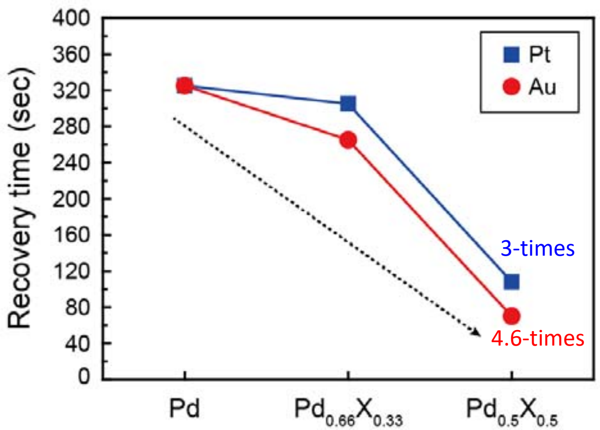
✓ Bimetallic interfaces induced faster dissociation of hydrogen gas

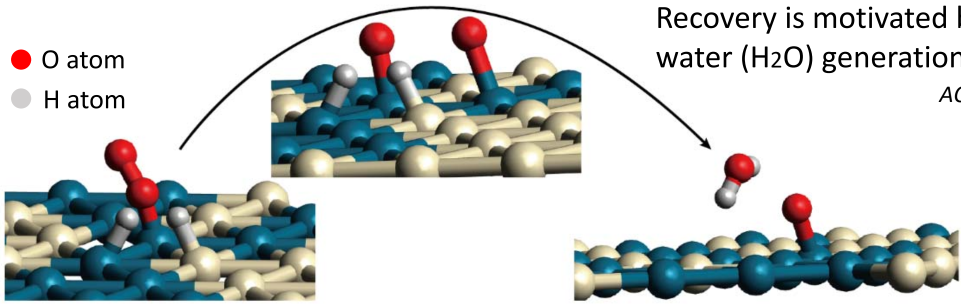
✓ Both adsorption and dissociation energies are larger in bimetallic interfaces compared to monometallic system

✓ Those larger energy resulted in faster response time

[MECHANSIM ANALYSIS – Faster Recovery Behavior]

- **Decrease of recovery time**



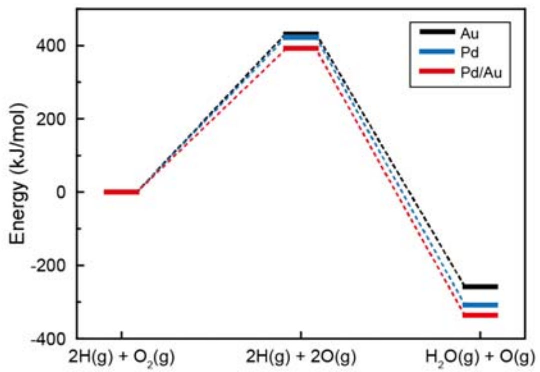


Recovery is motivated by water (H_2O) generation by air gas
ACS Nano **2015**

✓ Water generation using hydrogen and oxygen has lower intermediate energy in bimetallic system compared to monometallic system

✓ Accordingly, oxygen in air gas fast makes water with dissociated hydrogen on bimetallic interfaces

[Au/Pd case]



[Pt/Pd case]