

Low-Temperature Catalytic CO Oxidation

We are focused mainly on:

- **Supported Au nanoparticles**
- **Supported or promoted CuO systems**
- **Unsupported and supported CoO_x catalysts**

Low-temperature CO oxidation in environmental and industrial catalysis

- ❑ Engine-out emissions control for advanced vehicles with homogeneous charge compression ignition (HCCI) engines
- ❑ Reformer product purification for polymer electrolyte fuel cells
- ❑ Indoor air cleaning
- ❑ Gas sensors
- ❑ Gas masks
- ❑ Prevention of the deactivation of CO₂ lasers

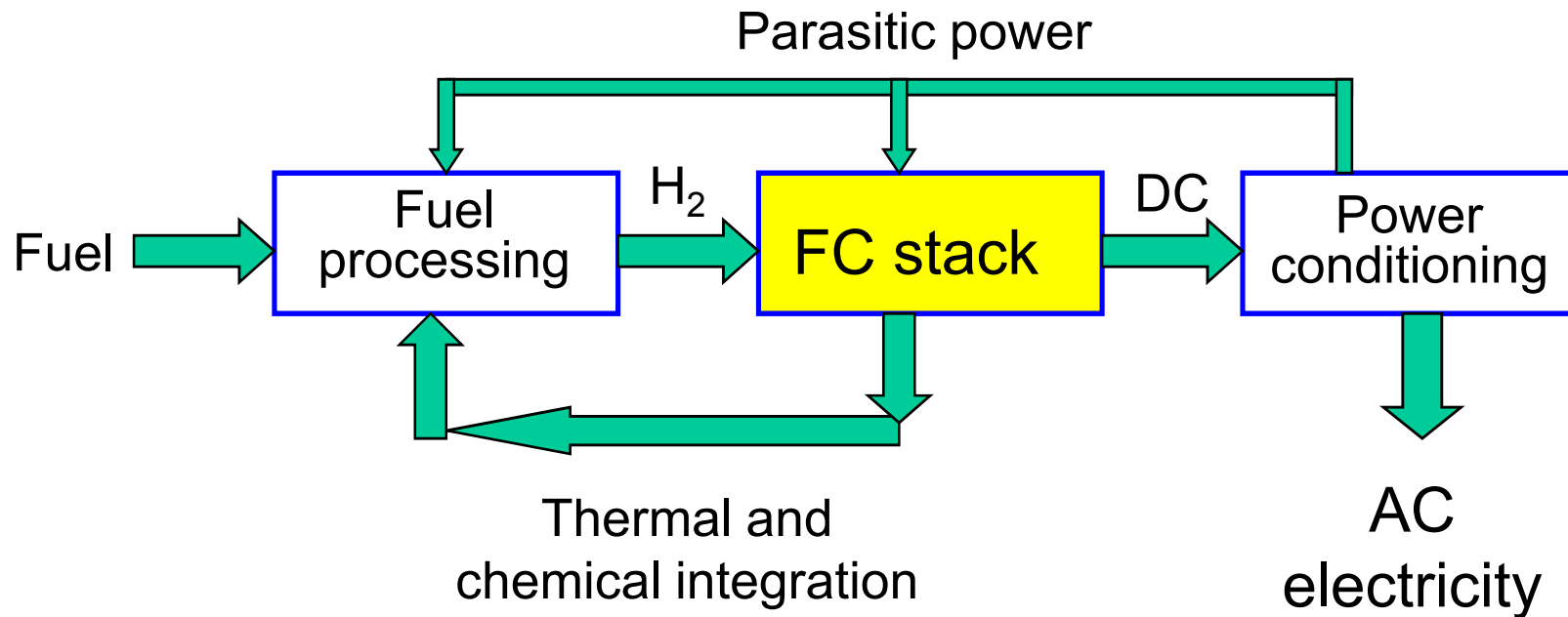
Low-temperature CO oxidation for fuel cells applications

The need of low-temperature CO oxidation in fuel cell road applications

Hydrogen-fuelled polymer electrolyte membrane fuel cells, representatively proton-exchange membrane fuel cells (PEMFCs), have been recognized to be the most environmentally-benign energy conversion system for road vehicle applications in the near future. The on-board production of H₂ from less explosive gaseous or liquid hydrocarbons using a systematic combination of catalytic steam reforming processes with a water-gas shift reaction needs to overcome some technical barriers associated with the distribution and storage of H₂ for commercialization of the fuel cell systems.

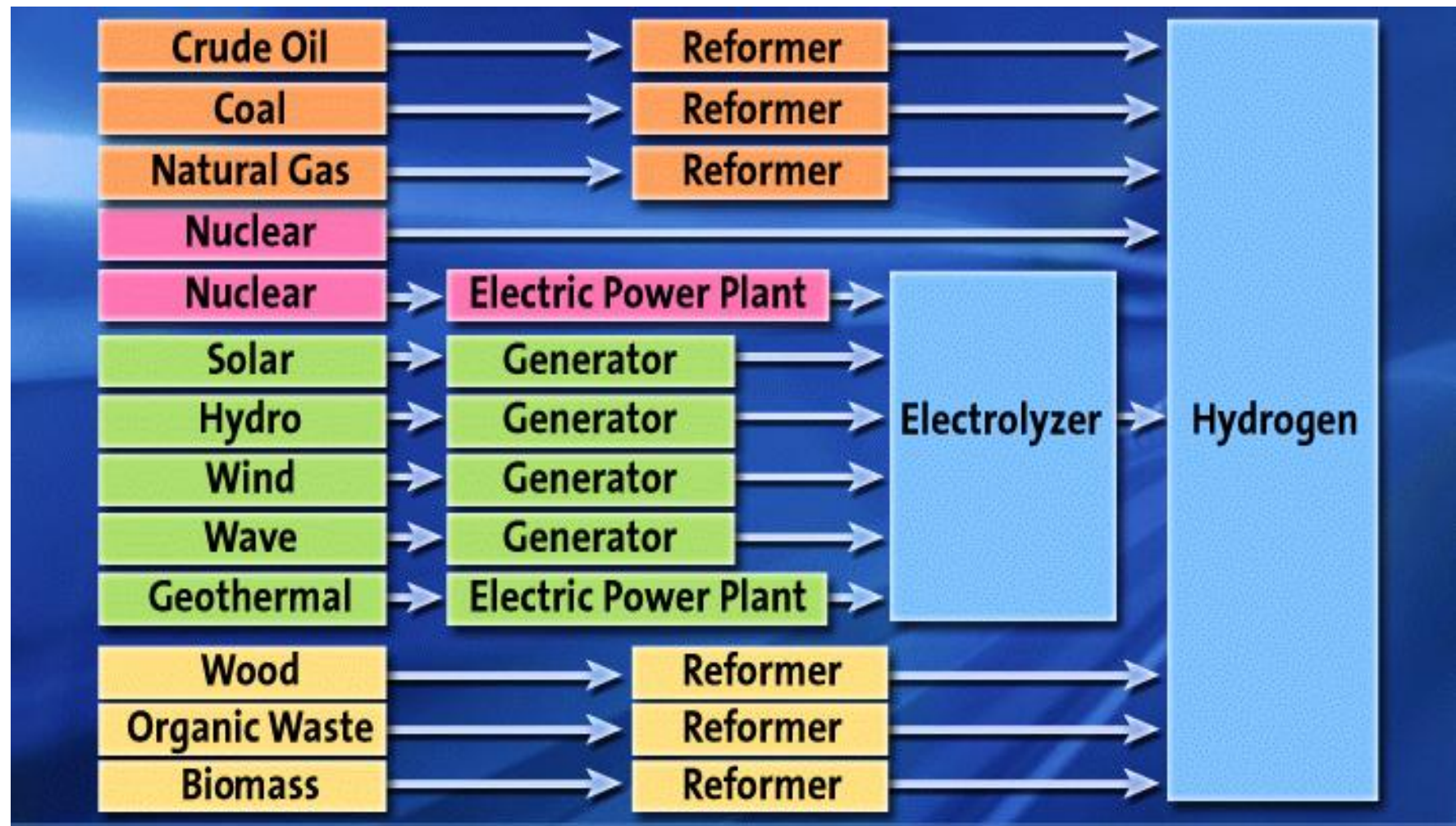
The reformer gas products contain large amounts of CO (typically 0.5 – 2%) by which anodic Pt electrocatalysts in the fuel cell systems are known to be significantly deactivated. In an attempt to lower CO in H₂-rich gas streams to acceptable levels less than 100 ppm, preferential oxidation (designated to “PrOx”) of CO has been extensively studied using a variety of catalysts that must possess high activity and selectivity in the temperature range of 70 – 300°C because the PrOx catalysts are placed between the reformer and the fuel cell system operated at the respective temperatures ranging from 70 – 130 and 200 – 300°C.

Schematic of fuel cell system

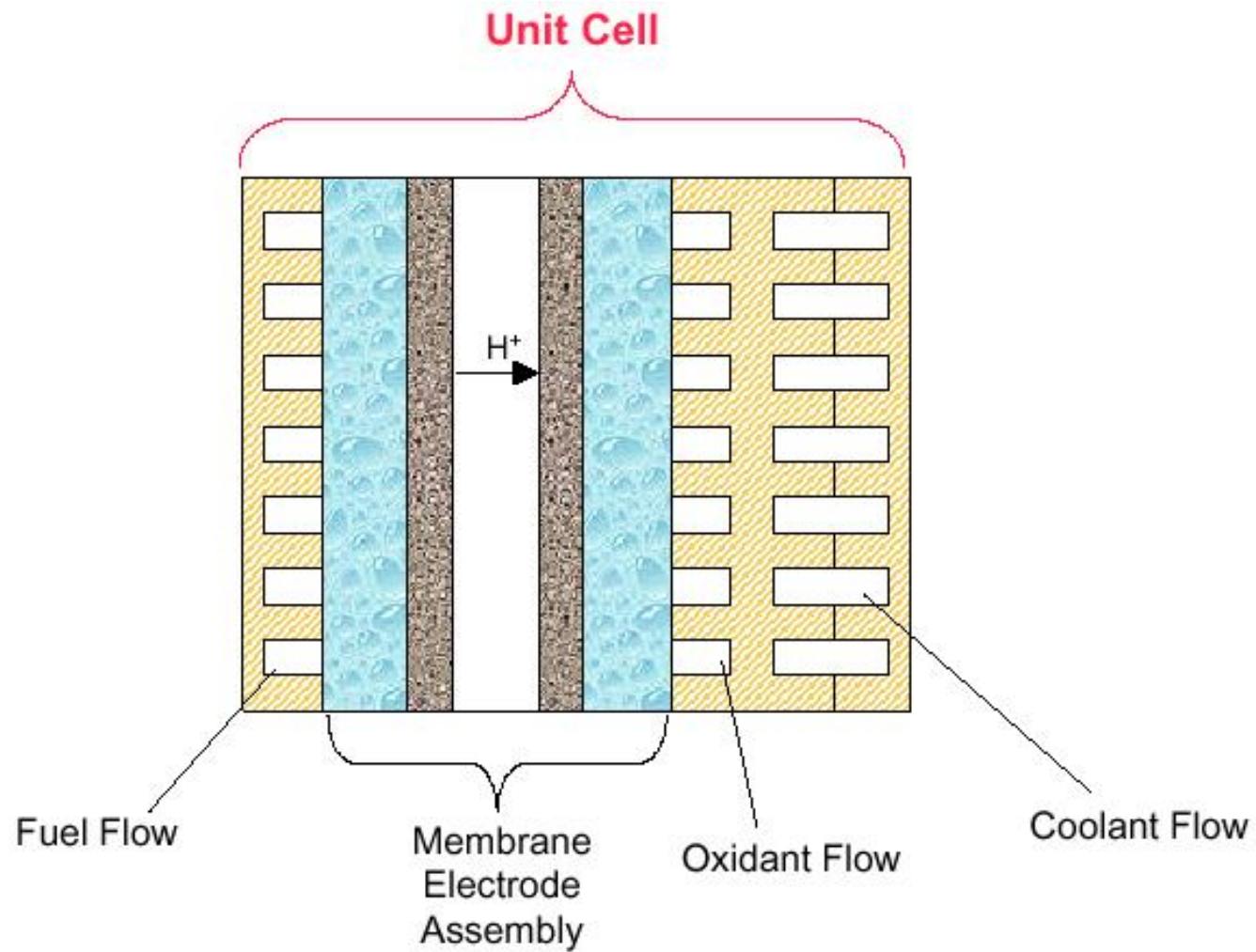


An electrochemical engine produces electricity from a fuel.

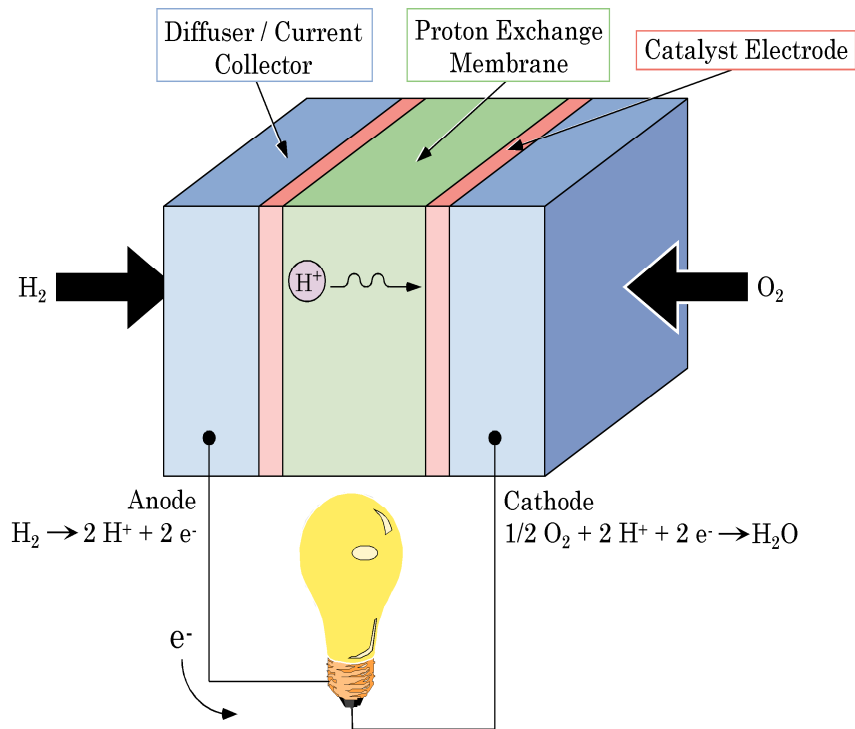
Pathways of producing H₂



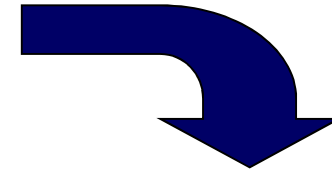
Unit cell structure of PEM fuel cells



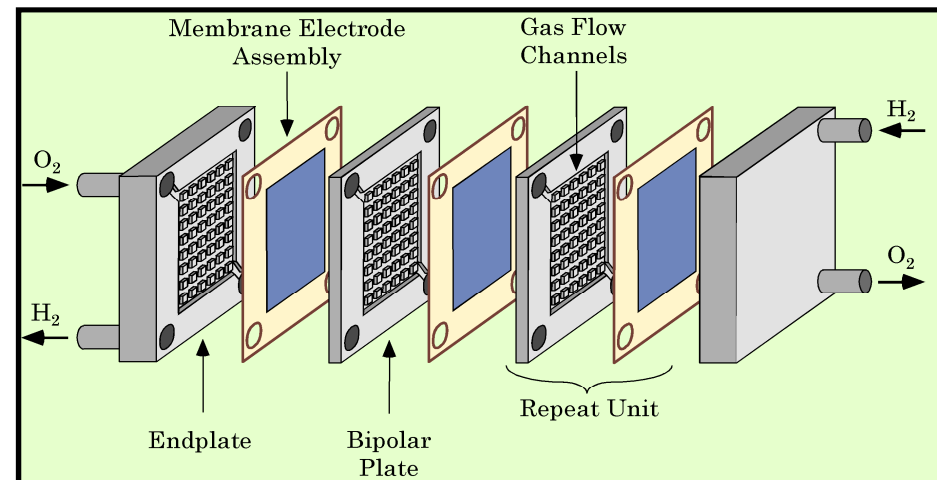
How do PEMFCs work?



Single Fuel Cell

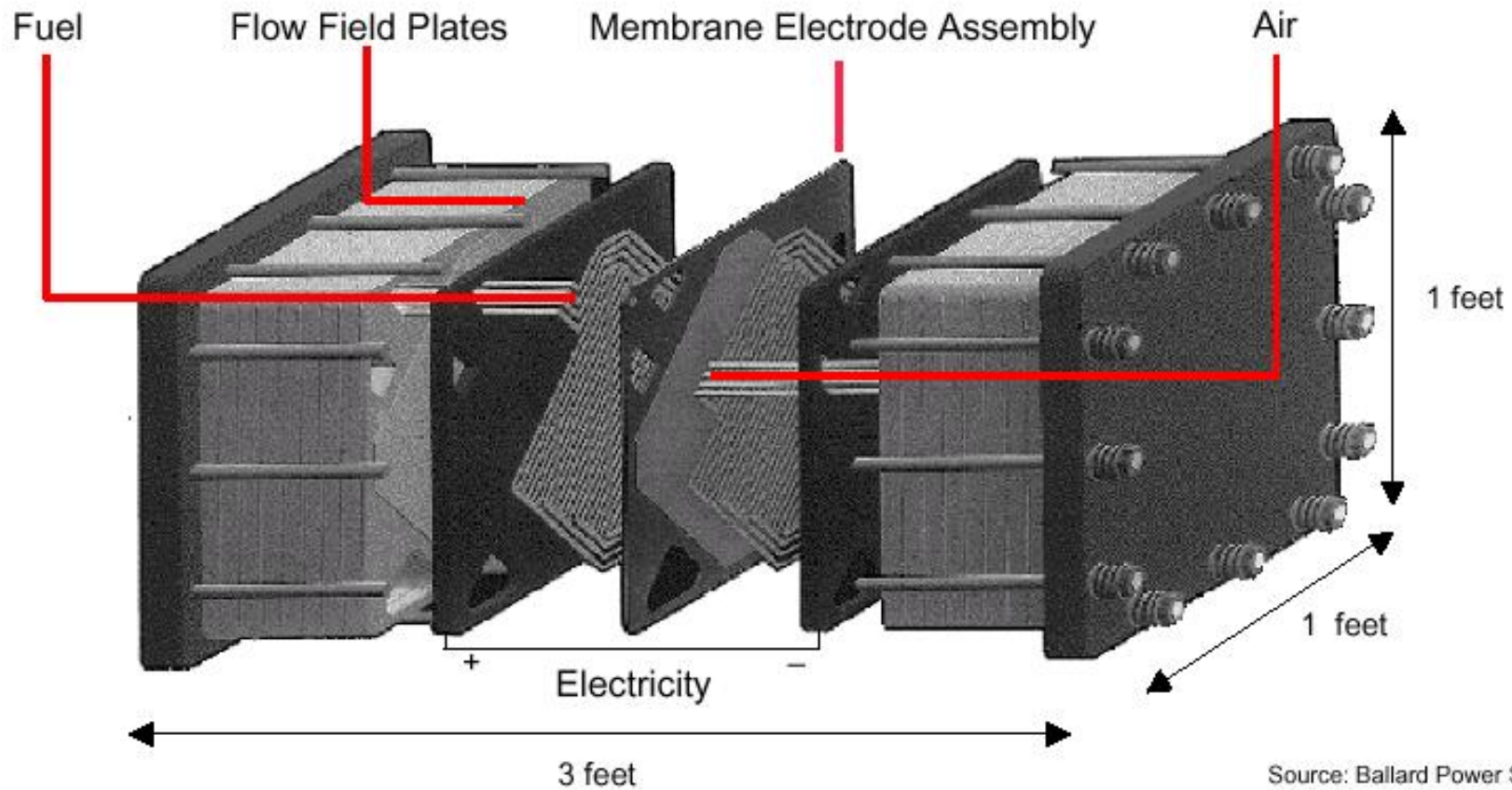


Fuel Cell Stack



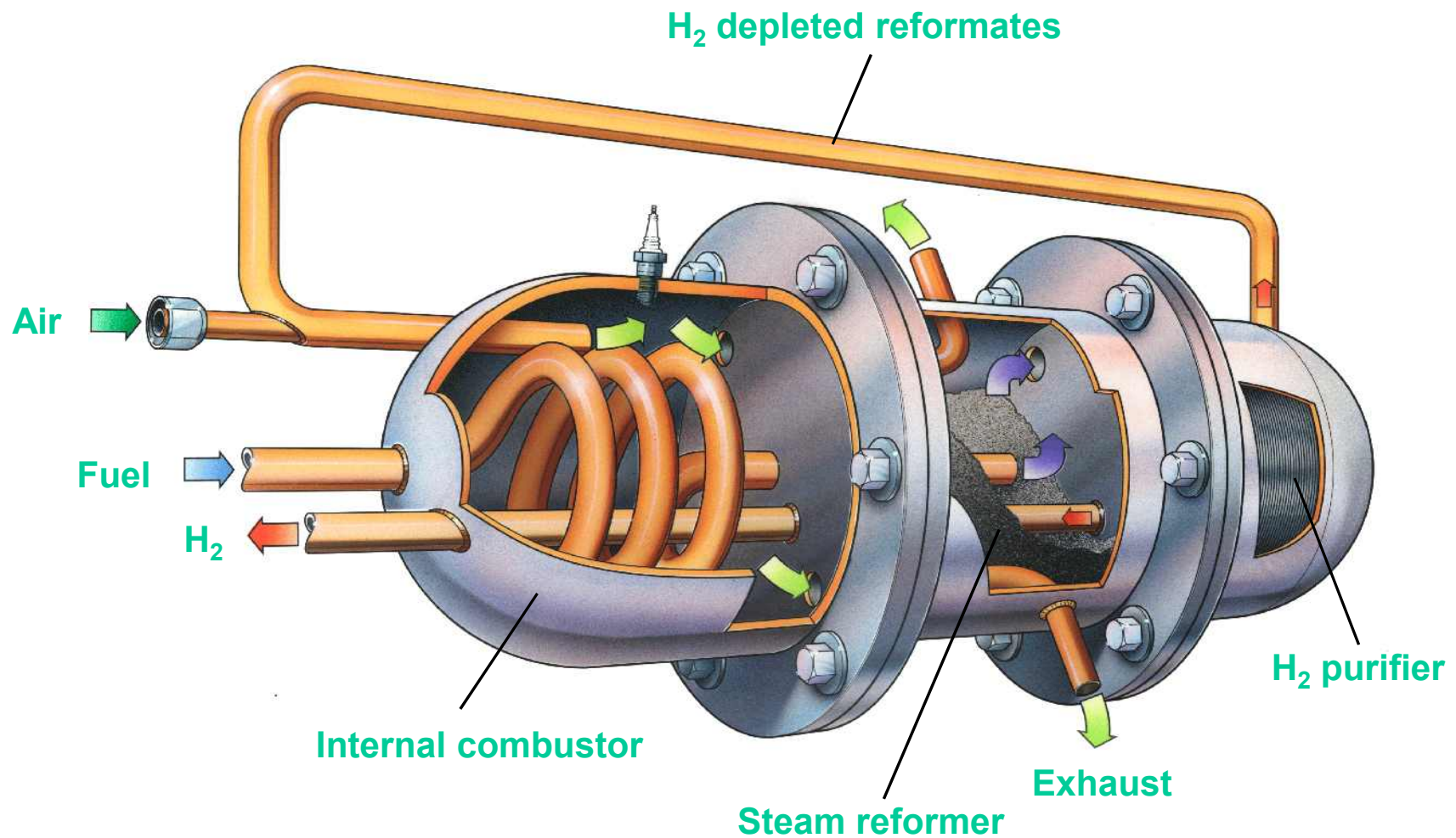
Fuel Cells produce electricity through the electrochemical oxidation of H_2 over Pt-based electrocatalyst.

Stack structure of PEM fuel cells



Source: Ballard Power Systems

An integrated fuel processor for PEMFCs applications



Typical end products of fuel reformers for PEMFCs

Gas composition and operating temperature window	PEMFC
CO (%)	0.5 ~ 2
H ₂ (%)	45 ~ 75
CO ₂ (%)	15 ~ 25
H ₂ O (%)	15 ~ 30
NO _x (ppm)	n.d.
HC ^a (%)	trace
PM (mg/m ³)	n.d.
T (°C)	70 ~ 300

^a Unconverted or burned.

- Reforming reactions of HCs and alcohols are required to produce H₂ for PEMFCs.
- The concentration of CO from the fuel reformers must be less than 100 ppm to prevent and/or lower the deactivation of Pt-based electrocatalysts in the PEMFCs.

Energy density of typical fuels

Fuel	Energy produced during combustion (kJ/g)
Hydrogen gas (H ₂)	143
Methane gas (CH ₄)	56
Petrol (Octane, C ₈ H ₁₈)	48
Coal (Carbon, C)	33
Ethanol (C ₂ H ₅ OH)	30
Methanol (CH ₃ OH)	23
Carbohydrates (e.g. C ₆ H ₁₂ O ₆)	16
Carbon monoxide gas (CO)	10

Hydrogen refueling station in Germany



Fear of hydrogen's explosiveness

Hydrogen Fuel Leak, 3.4 lbs
175,000 BTU

Gasoline Fuel leak 5 liters
70,000 BTU

- Comparison of fuel leaks
- Hydrogen fuel leak with all fail safes disengaged.

The safety in handling and storages is a big challenge to the widespread use of H₂.



PEM fuel cell anode feed gas specifications

Component	Specification	Comments
Hydrogen	50–100%	Cell performance not adversely effected by moderate dilution
CO	max. 10–100 ppm	Severe poison to electrocatalyst (partly reversible) Tolerance level dependent on cell design and operating conditions.
N ₂ , CO ₂	0–50%	Relatively inert
Water	Variable	Humidification necessary. Requirements vary with electrode design.
Methane	0% desirable	Relatively inert
Formic acid	0%	Severe poison (irreversible)
Methanol	0% desirable	Reversible performance loss at 5000 ppm
Formaldehyde	0% desirable	Reversible performance loss at 5000 ppm
Methyl formate	0% desirable	Reversible performance loss at 5000 ppm

Amphlett et al., Int. J. Hydrogen Energy, 12 (1996) 673.

Catalysts employed for CO conversion

Composition and BET specific surface areas of the Au/ α -Fe₂O₃, CuO–CeO₂ and Pt/ γ -Al₂O₃ catalysts

Catalyst	Composition	BET specific surface area (m ² g ⁻¹)
Au/ α -Fe ₂ O ₃	2.9 wt.% Au	49.8
CuO–CeO ₂	1.9 wt.% Cu	19.5
Pt/ γ -Al ₂ O ₃	5.0 wt.% Pt	224.0

Avgouropoulos et al., *Catal. Today*, 75 (2002) 157.

Total surface area by BET measurements

Metals surface area ?

Volumetric adsorption technique for metal surface area measurements

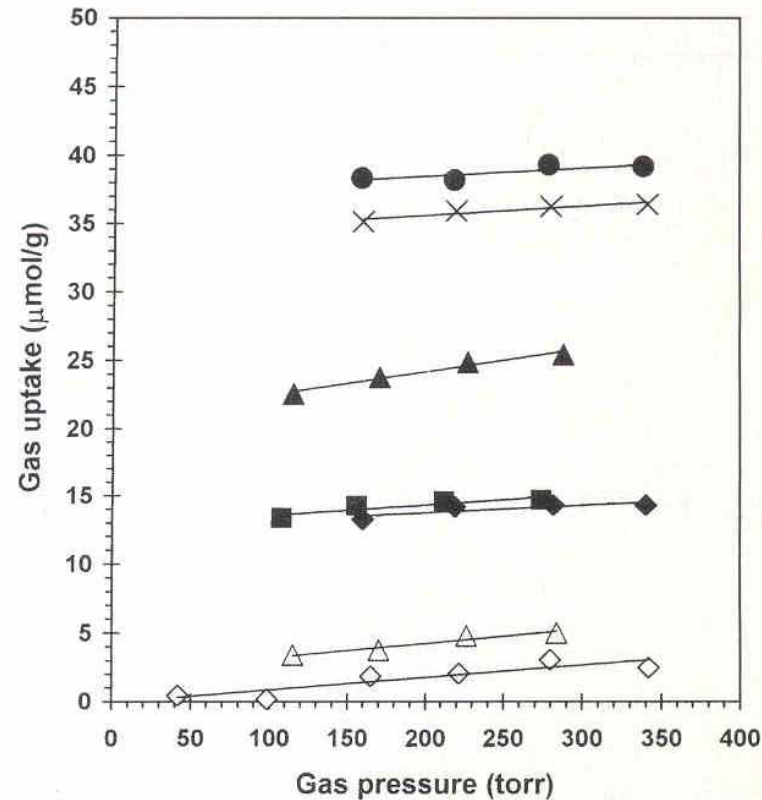


FIG. 1. Adsorption isotherms on 0.81% Pt/SiO₂ after either pretreatment II (HTR) or I (HTR). (●) H₂ titration-N₂O; (■) H₂ adsorption; (▲, △) CO adsorption; (◆, ◇) O₂ adsorption; (×) H₂ titration-O₂. Open and closed symbols present the respective total and reversible gas uptakes at 300 K.

Kim et al., J. Catal., 204 (2001) 348.

How has a Pt_s fraction been determined to date?



- One-to-one stoichiometry.
- Independent of Pt crystallite sizes.



- $O/Pt_s = 1$ ($O/Pt_s = 0.5$).
- Dependent on Pt crystallite sizes.



- $CO_{irr}/Pt_s = 1$ ($CO_{irr}/Pt_s = 0.5$).
- Dependent on Pt crystallite sizes.

Determination of metal dispersion and surface area

Sample	Pretreatment	Gas uptake ($\mu\text{mol/g}$)						Dispersion based on ^b					
		H ₂ -N ₂ O titr	H ₂ Tot	O ₂ Irr	CO Irr	H ₂ -O ₂ titr	"O" ^a	$\frac{H_{\text{titr}}-N_2O}{Pt}$	$\frac{H_{\text{tot}}}{Pt}$	$\frac{O_{\text{irr}}}{Pt}$	$\frac{CO_{\text{irr}}}{Pt}$	$\frac{O}{Pt}$	$\frac{H_{\text{titr}}-O_2}{Pt}$
A	II (HTR)	37.3 ± 0.1						0.60					
	I (HTR)		12.7 ± 0.1	11.3 ± 0.1	18.6 ± 0.2	34.5 ± 0.2	24.2 ^c		0.61	0.55	0.45	0.58	0.55
				11.4 ± 0.1 ^c		34.1 ± 0 ^d				0.55 ^c			0.55 ^d
B	II (HTR)	37.7						0.60					
C	I (HTR)		12.7 ± 0.1						0.61				
D	I (HTR)			11.6						0.56			
E	I (HTR)			11.4						0.55			
F	I (HTR)			11.3 ^c						0.54			
G	I (HTR)				18.3						0.44		
E	I (HTR)					34.2							0.55
F	I (HTR)					34.2 ^d							0.55 ^d

Note. No irreversible CO adsorption on pure SiO₂ after any pretreatment.

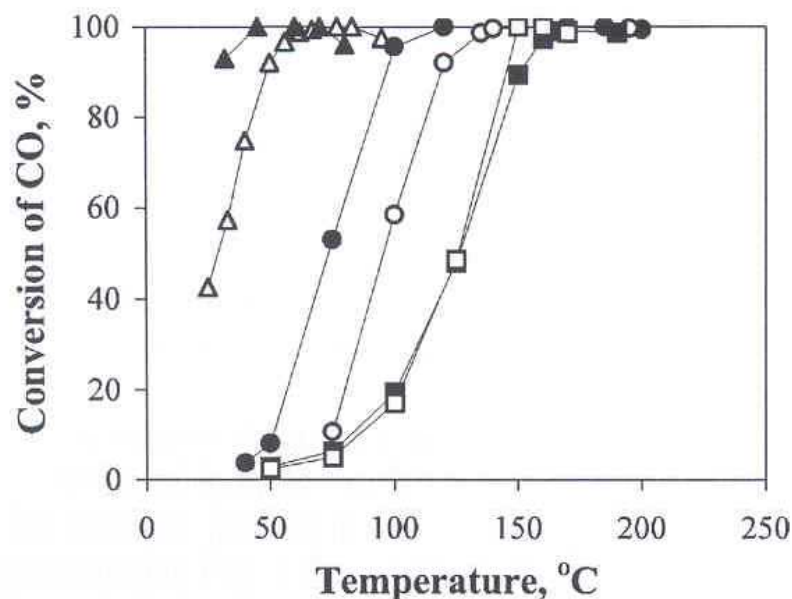
^a Atomic O via N₂O decomposition at 363 K measured gravimetrically.

^b Assuming H/Pt_s = O/Pt_s = CO/Pt_s = 1.

^c At 363 K.

^d H₂ titration at 300 K after exposure to O₂ at 363 K.

Effect of CO₂ on the catalytic CO conversion



Basical conditions:

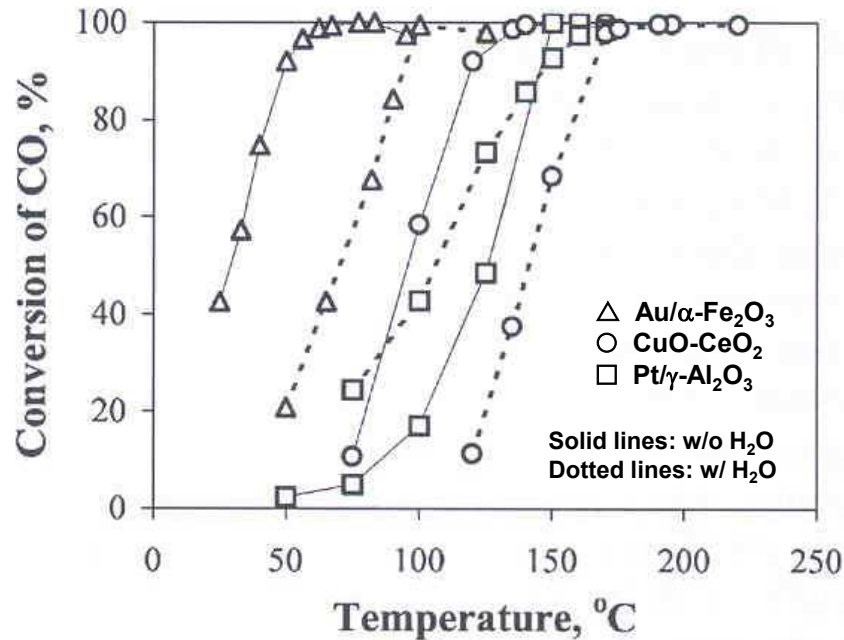
[CO] = 1%,

[O₂] = 1.25% and

[H₂] = 50%.

Fig. 2. Variation of the CO and O₂ conversion and of the selectivity with the reaction temperature for the selective oxidation of CO, at $W/F = 0.144 \text{ g s cm}^{-3}$, over the Au/α-Fe₂O₃ (Δ), CuO-CeO₂ (○), and Pt/γ-Al₂O₃ (□) catalysts in the absence of CO₂ (filled symbols) and in the presence of 15 vol.% CO₂ in the reactant feed (open symbols).

Effect of H₂O on the catalytic CO conversion



Basical conditions:

[CO] = 1%,

[O₂] = 1.25% and

[H₂] = 50%.

Fig. 3. Variation of the CO and O₂ conversion and of the selectivity with the reaction temperature for the selective oxidation of CO, at $W/F = 0.144 \text{ g s cm}^{-3}$, over the Au/α-Fe₂O₃ (Δ), CuO-CeO₂ (○), and Pt/γ-Al₂O₃ (□) catalysts in the presence of 15 vol.% CO₂ (solid lines) and in the presence of both 15 vol.% CO₂ and 10 vol.% H₂O in the reactant feed (dotted lines).

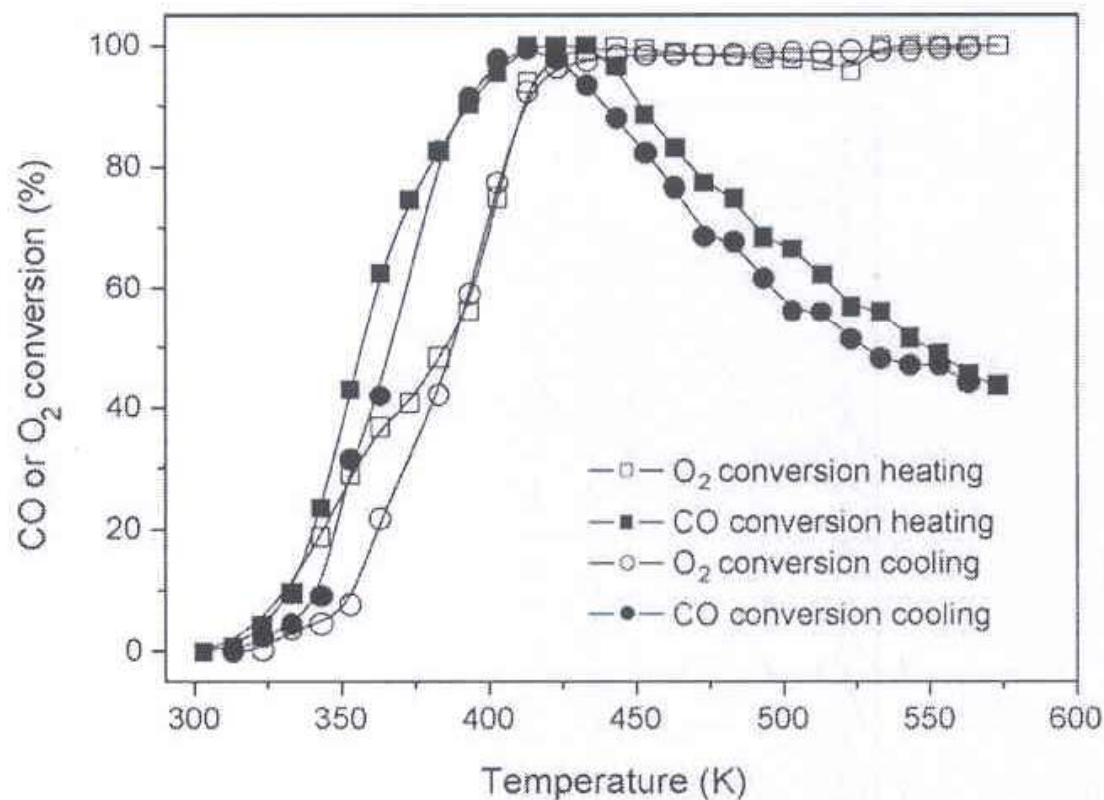
The water gas shift reaction occurs on the supported Pt metals:



Avgouropoulos et al., Catal. Today, 75 (2002) 157.

CO oxidation over a 1 wt% CuO/CeO₂ catalyst

After calcination at 773 K in air for 2 h



Reaction conditions:

[CO] = 1%,

[O₂] = 1.25% and

[H₂] = 50%.

-The deactivation is associated with:

accumulation of hydroxyls on the interfacial active sites and/or

- sintering of CuO sites.

Martinez-Arias et al., Appl. Catal. B, 65 (2006) 207.

CO oxidation over CuO/CeO₂ catalysts

After calcination at 450°C in air for 4 h

Reaction conditions: [CO] = 1% and [O₂] = 1%.

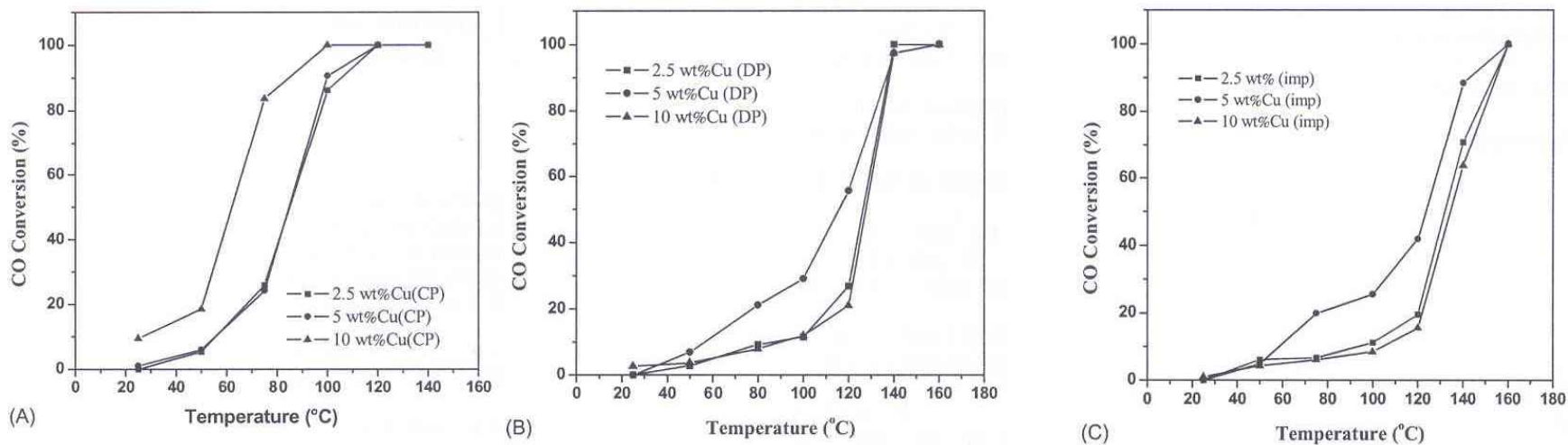


Fig. 6. Effect of copper loading on the CO oxidation for CuO/CeO₂ catalysts prepared by (A) co-precipitation; (B) deposition-precipitation; (C) impregnation; (■) 2.5 wt.% Cu; (●) 5 wt.% Cu; (▲) 10 wt.% Cu.

Tang et al., Catal. Today, 93 (2004) 191.