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CARBON DIOXIDE POISONING ON PROTON-EXCHANGE-MEMBRANE FUEL CELL ANODES

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Carbon dioxide poisoning on proton-exchange-membrane fuel cell anodes

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Carbon dioxide, which is present in reformate fuels in concentrations up 25%, can have a detrimental effect on the fuel cell performance that goes beyond dilution effects associated with an inert gas. The origin of these poisoning effects is the reverse water gas shift reaction, i.e in a fuel cell CO_2 can be reduced by hydrogen adsorbed on the catalyst. This reaction results in an adsorbate on the anode catalyst. Fuel cell tests involving various Pt–based catalysts have shown that anode poisoning depends on the composition of the catalyst.

The carbon dioxide reduction on Pt-based carbon supported catalysts as a function of the electrode potential was studied using cyclic voltammetry and chronocoulometry. The results indicate the formation of adsorbed species (most likely, carbon monoxide) on the surface of all these catalysts. Closer inspection also revealed differences between the samples. From the kinetic data analysis it is clear that, unlike Pt/C, some bimetallic (PtM/C) catalysts also catalyse the oxidation of the adsorbed species to carbon dioxide at low overpotentials. This ensures a higher equilibrium concentration of the free sites on the surface of this type of catalysts compared to that on Pt/C.

Studies with a kinetic model have shown that main effect of CO_2 reduction is that a large part of the catalytic surface area becomes inactive for H_2 dissociation. Subsequent desorption of CO from the catalyst surface, transport down the gas channel, and subsequent re-adsorption of CO plays a minor role. The main reason for this is that a large blockage of the surface area inhibits further formation of CO in the reduction reaction. It was found that a high rate constant of this reaction increases the anode polarisation losses, as does a reduced rate constant of the hydrogen dissociation reaction. The effects are mitigated by a high ratio of the CO desorption and adsorption rate constants, as well as by a high CO electro-oxidation rate constant.

Keywords: PEM fuel cell, reformate gas, carbon dioxide reduction, electrocatalysis

Carbon dioxide poisoning on PEM fuel cell anodes

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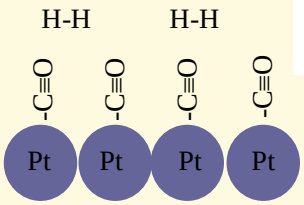
Poisoning by reformate gas:

- Reformate gas contains large amounts of CO_2 (order 25%) and small amounts of 10 - 50 ppm CO.
- Carbon monoxide poisoning:
  - very severe on Pt (> 1ppm)
  - PtRu, PtMo much more CO (tolerant 20-50 ppm)
- Carbon dioxide poisoning:
  - much smaller poisoning effect
  - tolerance also dependent on catalyst (PtMe)

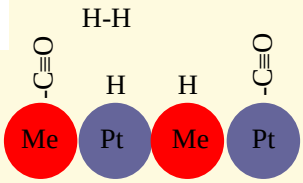
⇒ Are CO tolerant materials also CO_2 tolerant?

Pt-based catalysts for CO tolerance



$CO + {}^{*}_{Pt} \Leftrightarrow CO\text{-}{}^{*}_{Pt}$

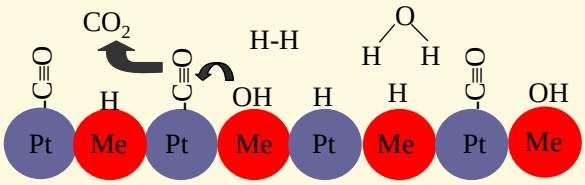
ligand effect



$H_2O + {}^{*}_{M} \Rightarrow OH\text{-}{}^{*}_{M} + H^{+} + e$

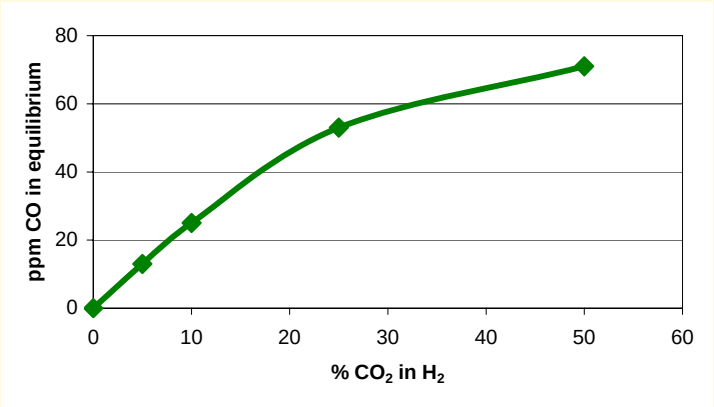
$CO\text{-}{}^{*}_{Pt} + OH\text{-}{}^{*}_{M} \Rightarrow CO_2 + H^{+} + e$

bifunctional mechanism



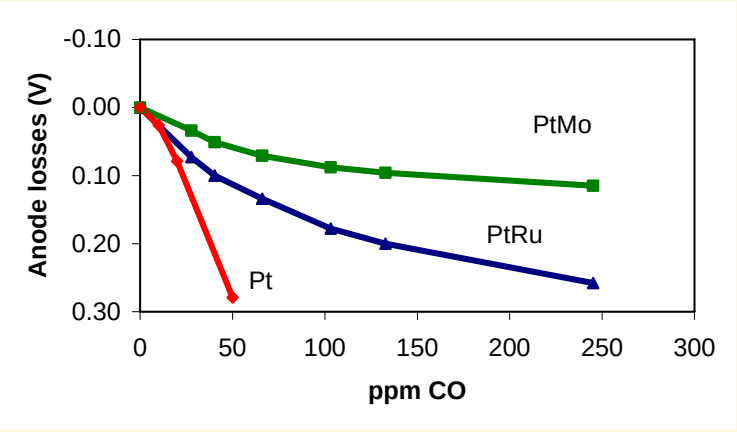
Reverse water gas shift equilibrium:

$$CO_2 + H_2 \leftrightarrow CO + H_2O$$



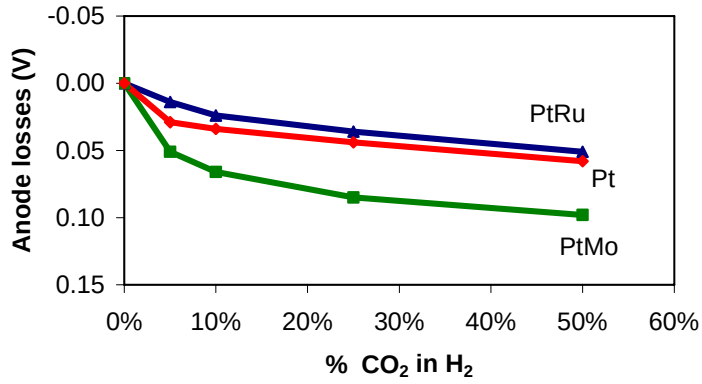
- 80oC, 1.5 bar, water saturated

CO tolerance: Pt < PtRu < PtMo



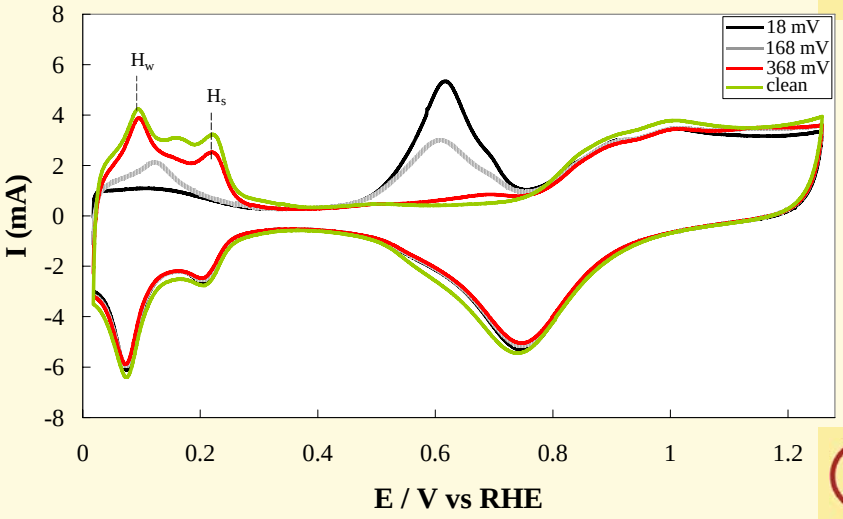
j= 350 mA/cm^2 , T=80^{o}C, ppm CO in H_2 (1.5 bar)
metal loading anode 0.4 mg/cm^2

CO_2 tolerance: PtMo < Pt < PtRu



j= 350 mA/cm^2 , T=80^{o}C, % CO_2 in H_2 (1.5 bar)
metal loading anode 0.4 mg/cm^2

CO_2 poisoning on Pt/C: cyclic voltammogram



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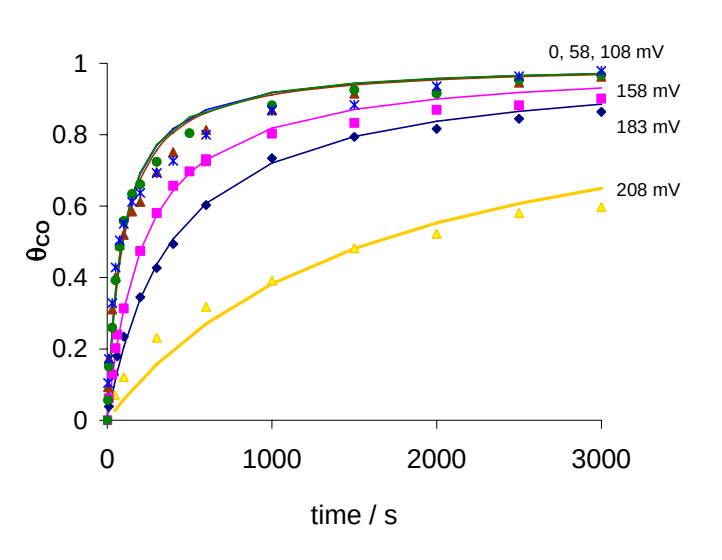
Mechanism in electrochemical cell:

Pt/C

$$H^+ + e \rightarrow H_{ad}$$
$$CO_2 + 2H_{ad} \rightarrow CO_{ad} + H_2O$$

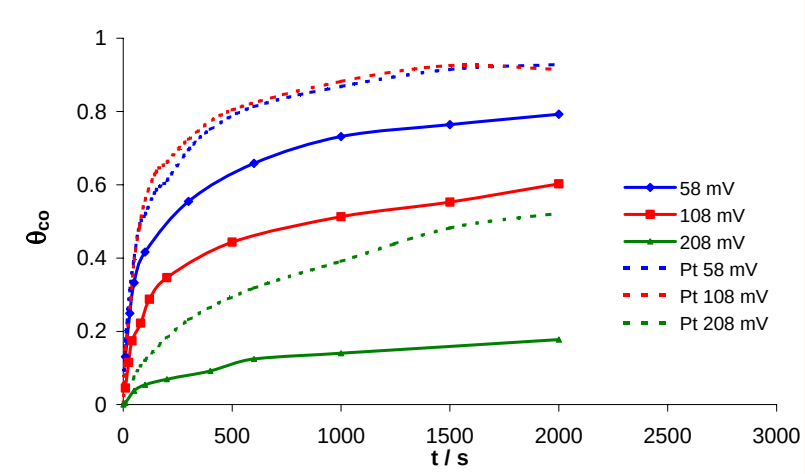
$$\frac{d\theta_{CO}}{dt} \approx \theta_H^2 \quad \theta_H = f(\eta)$$
$$\frac{d\theta_{CO}}{dt} = k(\eta)(1-\theta_{CO})^2$$

Kinetics of CO_2 reduction on Pt/C



CO_2 reduction on Pt/C in CO_2-saturated 0.5 M H_2SO_4

Kinetics of CO_2 reduction on PtMo/C



CO_2 reduction on Pt/C in CO_2-saturated 0.5 M H_2SO_4

Mechanism in electrochemical cell:

Pt/C

$$H^+ + e \rightarrow H_{ad}$$
$$CO_2 + 2H_{ad} \rightarrow CO_{ad} + H_2O$$

CO_2 reduction occurs : steady-state $\theta_{CO} = 1$ & $\theta_{free} = 0$

PtMo/C

$$H^+ + e \rightarrow H_{ad}$$
$$CO_2 + 2H_{ad} \rightarrow CO_{ad} + H_2O$$
$$CO_{ad} + H_2O \rightarrow CO_2 + 2H^+ + 2e$$

CO oxidation as well: steady-state $\theta_{CO} < 1$ & $\theta_{free} > 0$

$\Rightarrow$ No evidence for faster CO_2 reduction

Fuel Cell Anode Reactions/ Reformate Gas

$$H_2 \rightarrow 2H_{ad} \qquad k_a$$
$$H_{ad} \rightarrow H^+ + e$$

$$CO \leftrightarrow CO_{ad} \qquad k_{dc}/k_{ac}$$
$$CO_{ad} + H_2O \rightarrow CO_2 + 2H^+ + 2e \qquad k_{ec}$$

$$CO_2 + 2H_{ad} \rightarrow CO_{ad} + H_2O \qquad k_{rs}$$

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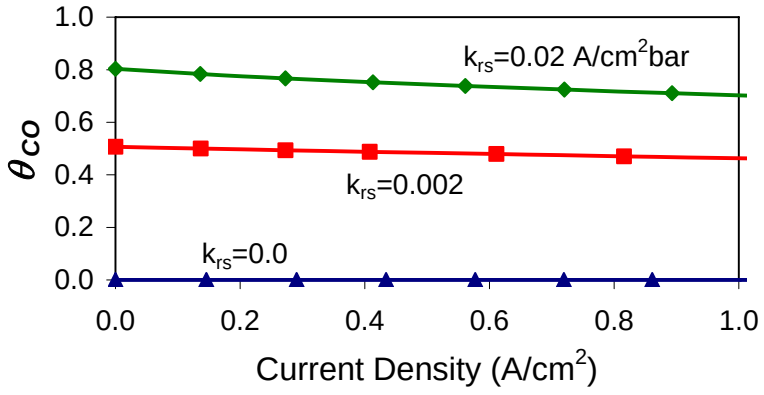
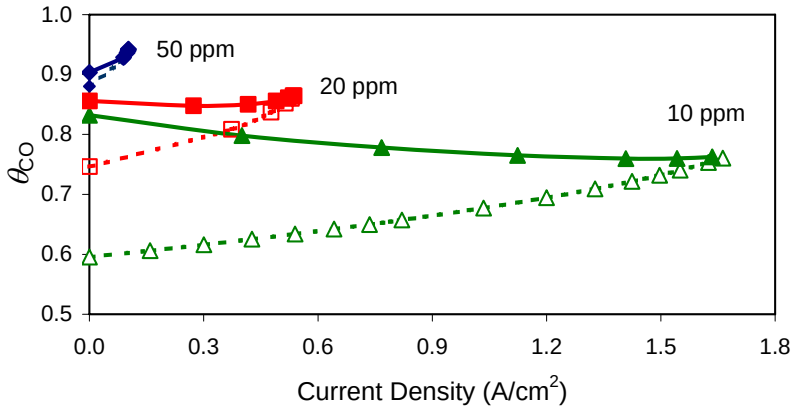
Model results: CO coverage
0.8 H_2 / 0.2 CO_2



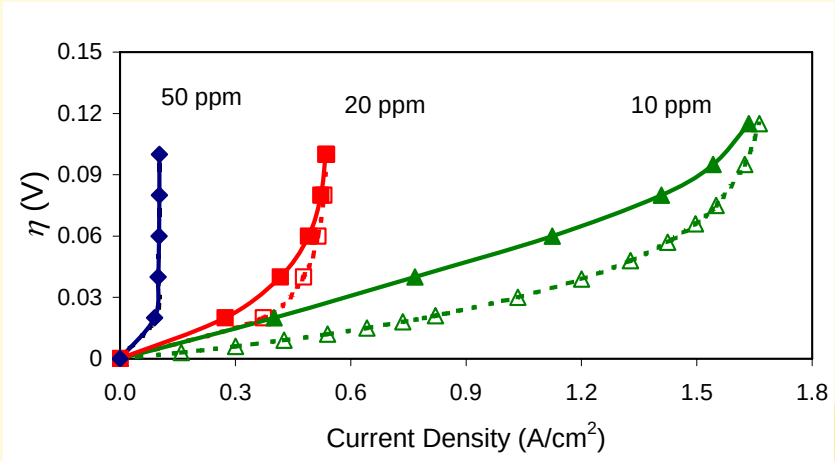
$$\theta_{CO} = \frac{k_{rs} pCO_2}{k_{dc} + k_{ec} \exp(\eta / b_c)} \theta_H^2$$

Model results: CO coverage
(0.8 H_2 /0.2 CO_2 /CO)

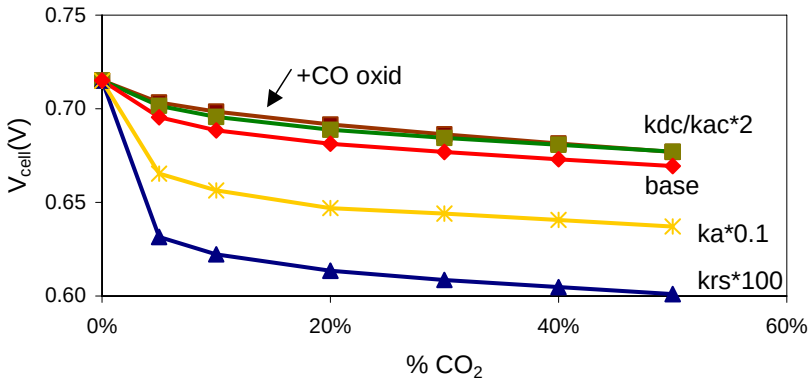


Dotted: H_2/CO Drawn: 80% H_2 / 20% CO_2 / CO

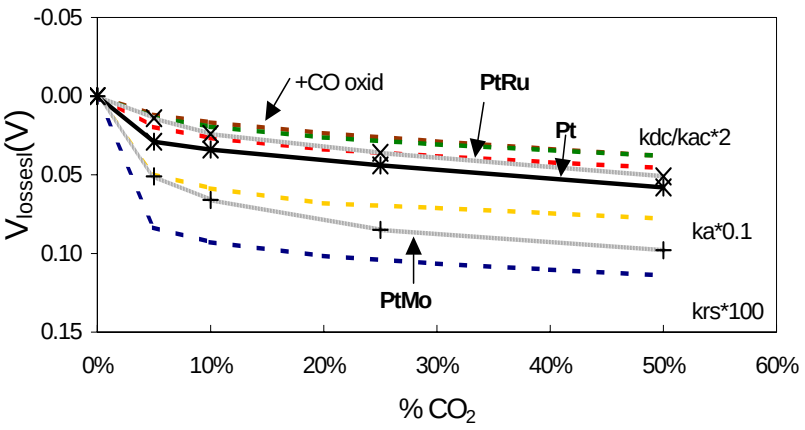
Polarisation curves



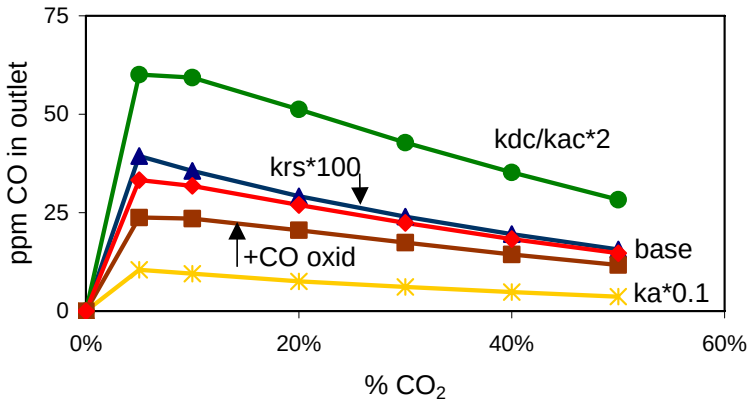
Model results: H_2/CO_2 feed



Comparison with experiment



Model results: CO in outlet (fixed H_2 stoichiometry)



CO_2 poisoning: conclusions

- Mechanism:
  - CO_2 reduction product poisons catalyst
  - non-electrochemical reaction with H_{ad}
- Modelling results:
  - CO_2 poisoning important at low CO content, decreases with current density
  - H_2/ CO_2: no relation poisoning effect and resulting CO content in flow
- CO tolerant catalysts not always more CO_2 tolerant
  - PtRu more CO_2 tolerant than Pt due to ligand effect
  - PtMo less tolerant: reduced H_2 dissociation rate suspected

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