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CO oxidation and CO_2 reduction on carbon supported $PtWO_3$ catalyst

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Presented at the 7th Spring Meeting of ISE, 22-25 March 2009, Szczyrk, Poland

ECN-L--09-179 December 2009

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CO oxidation and CO_2 reduction on carbon supported $PtWO_3$ catalyst

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Motivation

- PEM fuel cells are attractive power source
- H_2 - O_2 as fuel, Pt as a catalyst

however

- H_2 often contains traces of CO
- reformate contains CO and up to 25% of CO_2

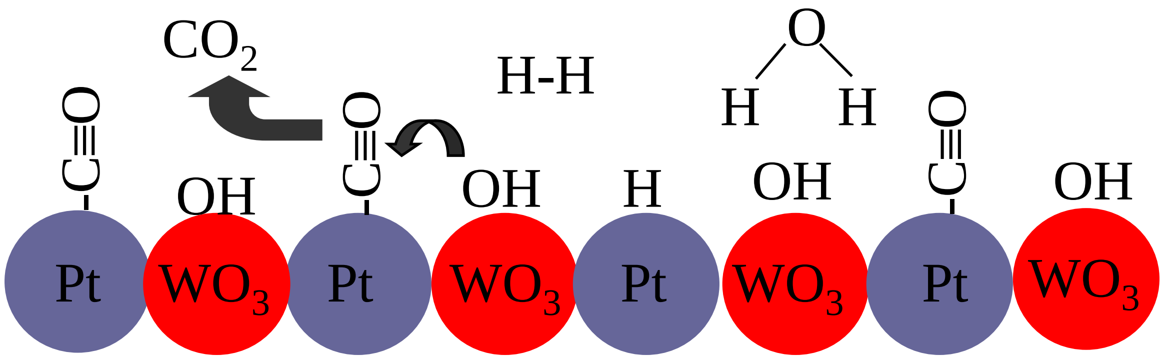
⇩

- **CO tolerance can be improved by alloying Pt-M**
- **CO_2 is often *not inert* then!**

Case study: $PtWO_3/C$

Why PtWO$_3$/C ?

- PtWO$_3$/C is a CO tolerant catalyst
- CO tolerance is through bifunctional mechanism



- Some report good performance in reformate-fed PEMFC
- Stability – WO$_3$ is insoluble in acids (PEMFC)

- Not as widely implemented as PtRu/C

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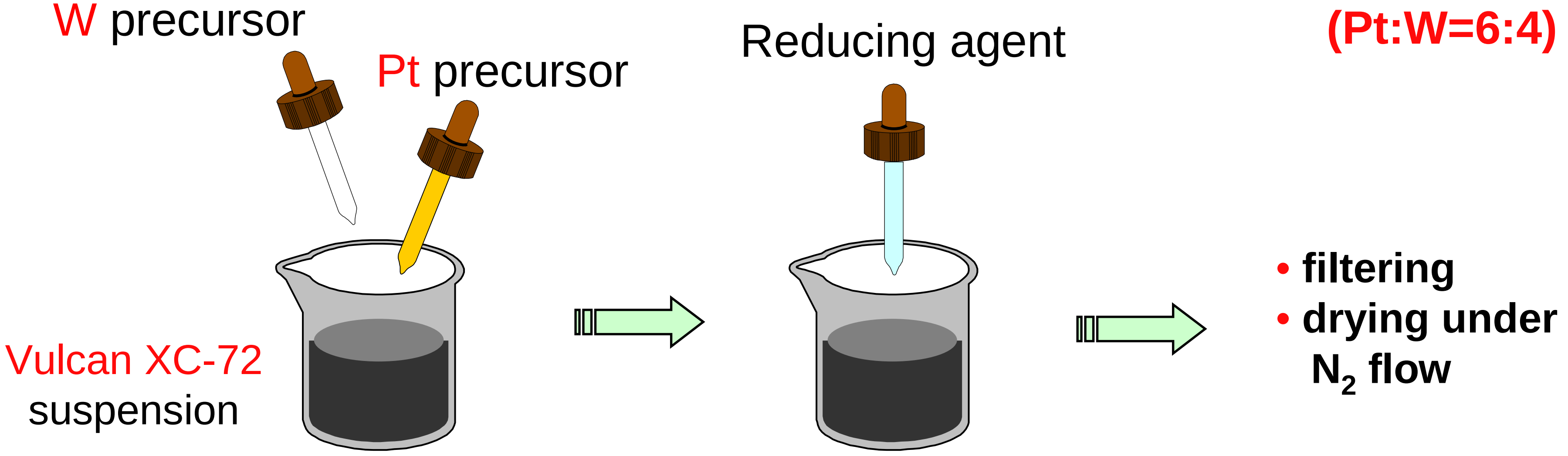
Catalyst preparation

Reductive co-precipitation



$PtWO_3/C$
(Pt:W=6:4)

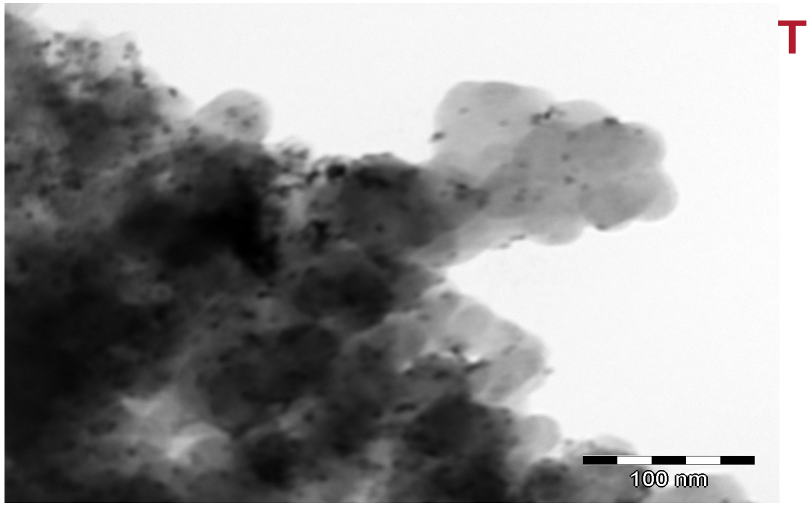
- **filtering**
- **drying under N_2 flow**

- **$H_2PtCl_6 \cdot xH_2O$**
- **$Na_2WO_4 \cdot 2H_2O$**

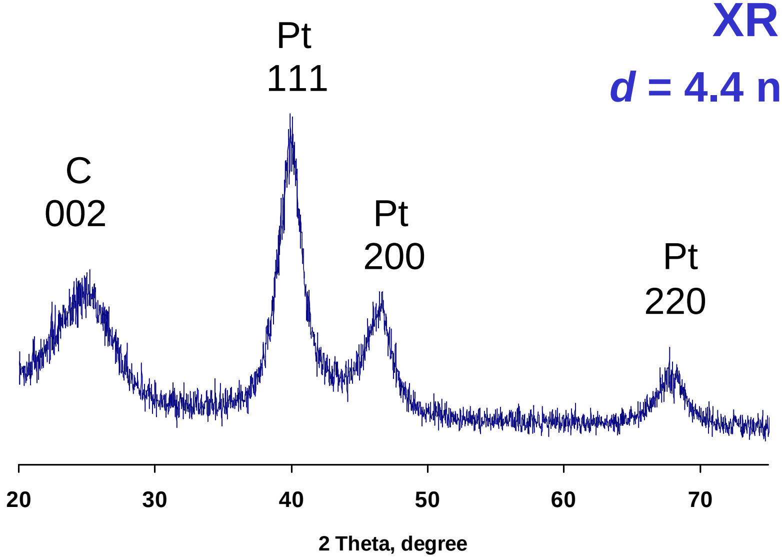
- **Formic acid**

US 006007934 A; PI 9702816-9 A

Catalyst characterisation

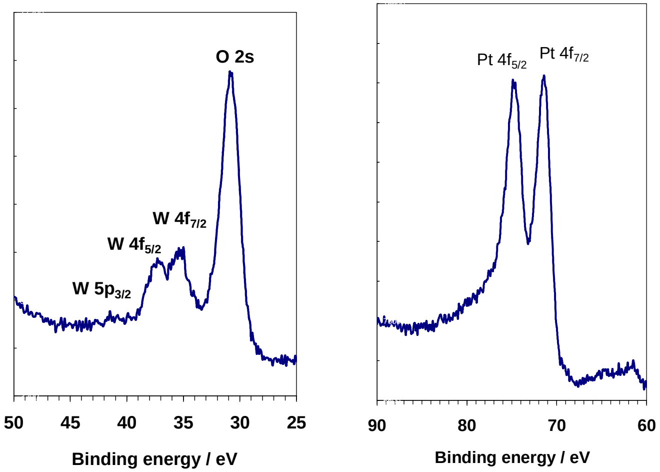


TEM



XRD

d = 4.4 nm

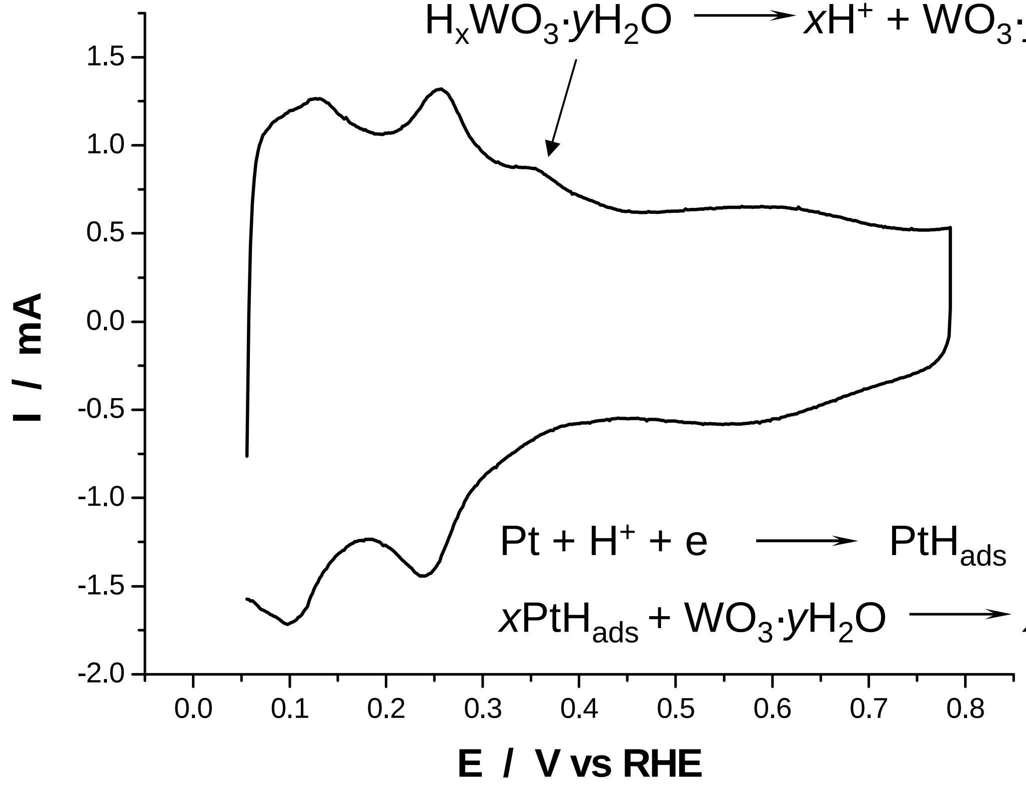


XPS

Pt is present as Pt metal
W as amorphous WO_3
no alloying Pt-W found

surface slightly enriched with WO_3
$Pt_{0.70}W_{0.30}$ (XPS) vs. $Pt_{0.77}W_{0.23}$ (EDX)

Catalyst characterisation



$PtH_{ads} \longrightarrow Pt + H^+ + e$

$H_xWO_3 \cdot yH_2O \longrightarrow xH^+ + WO_3 \cdot yH_2O + xe$

$Pt + H^+ + e \longrightarrow PtH_{ads}$

$xPtH_{ads} + WO_3 \cdot yH_2O \longrightarrow xPt + H_xWO_3 \cdot yH_2O$

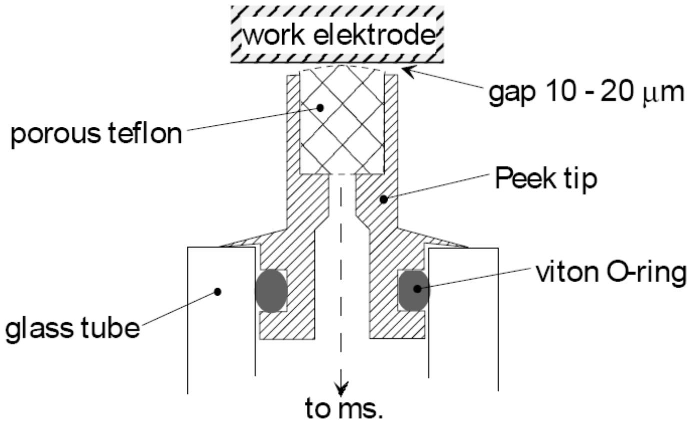
Bronze re-oxidation charge increases with scan rate decreasing
⇒ slow process

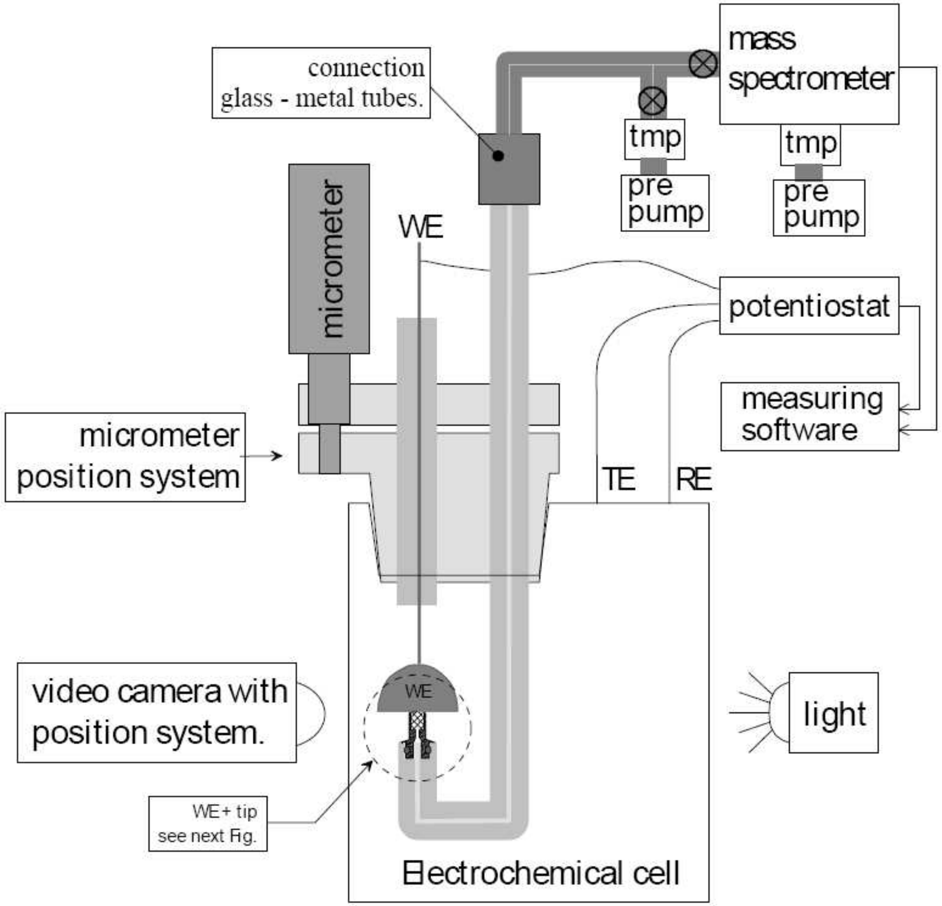
References:
Tseung, Kulesza,
Tsirlina, Kondo

$PtWO_3/C$, 0.5 M H_2SO_4;
10 mV/s

Catalyst characterisation

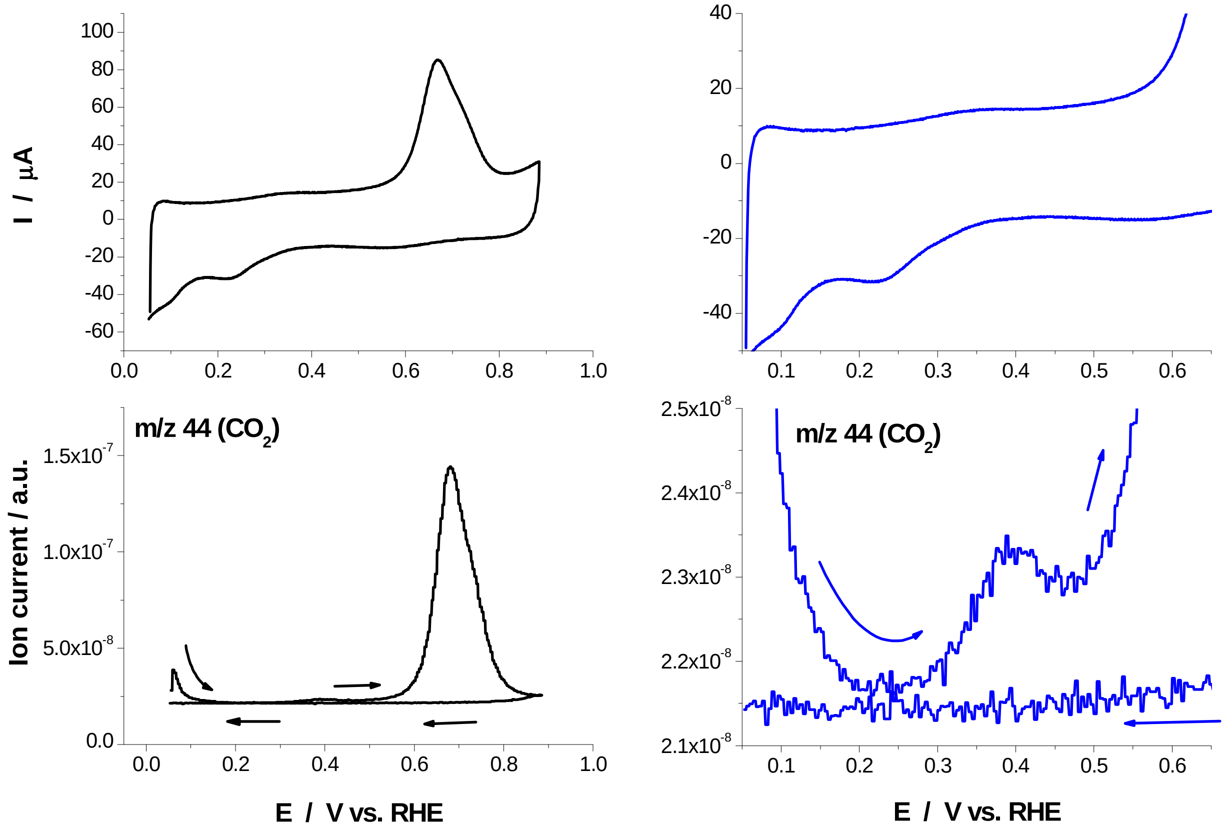
On-line electrochemical
mass spectrometry setup





A.H. Wonders, et al. J. Appl. Electrochem. 36 (2006) 1215

CO adlayer oxidation



Oxidation of a saturated adlayer of CO starts at low overpotentials, ~ 0.25 V

Small fraction of the adlayer, ca. 2 %, is being removed

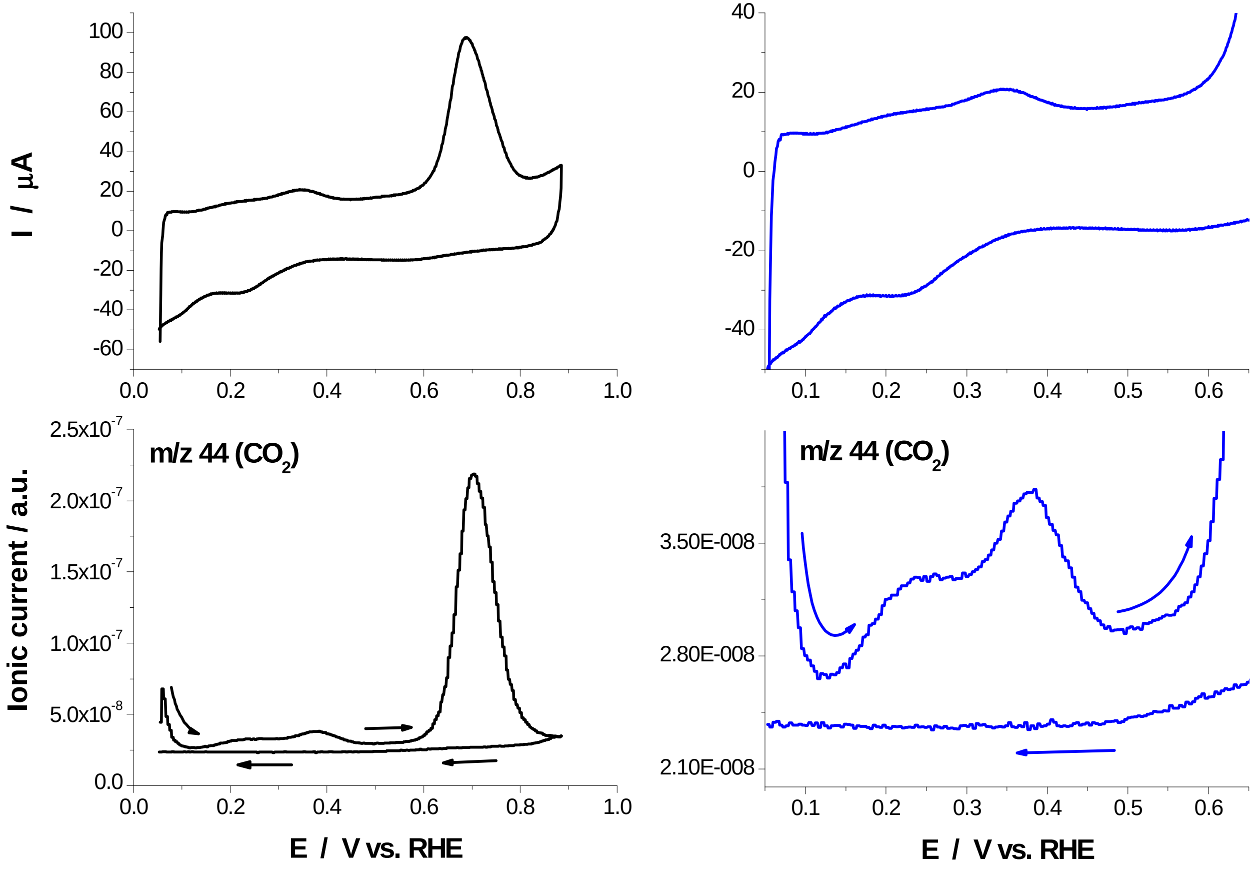
The major part oxidizes at potentials typical for Pt, ca. 0.7 V

On-line MS
0.5 M H_2SO_4; 2mV/s

saturated CO adlayer

T. Nagel et al, J. Solid State Electrochem., 7 (2003) 614.

Continuous CO oxidation



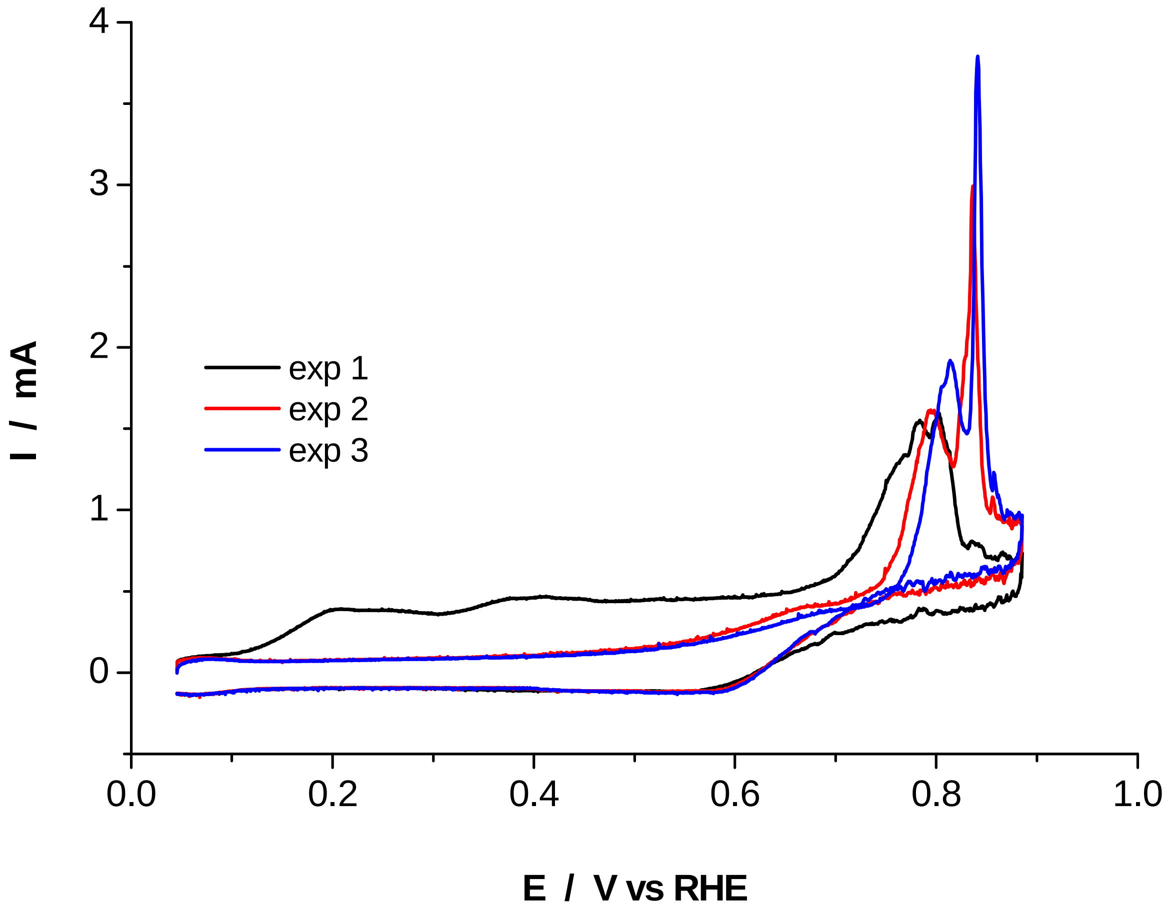
Oxidation of the dissolved CO on PtWO$_3$/C starts already at ~ 0.12 V vs. RHE

On-line MS
0.5 M H_2SO_4; 2mV/s

saturated CO solution

T. Nagel et al, J. Solid State Electrochem., 7 (2003) 614.

Continuous CO oxidation



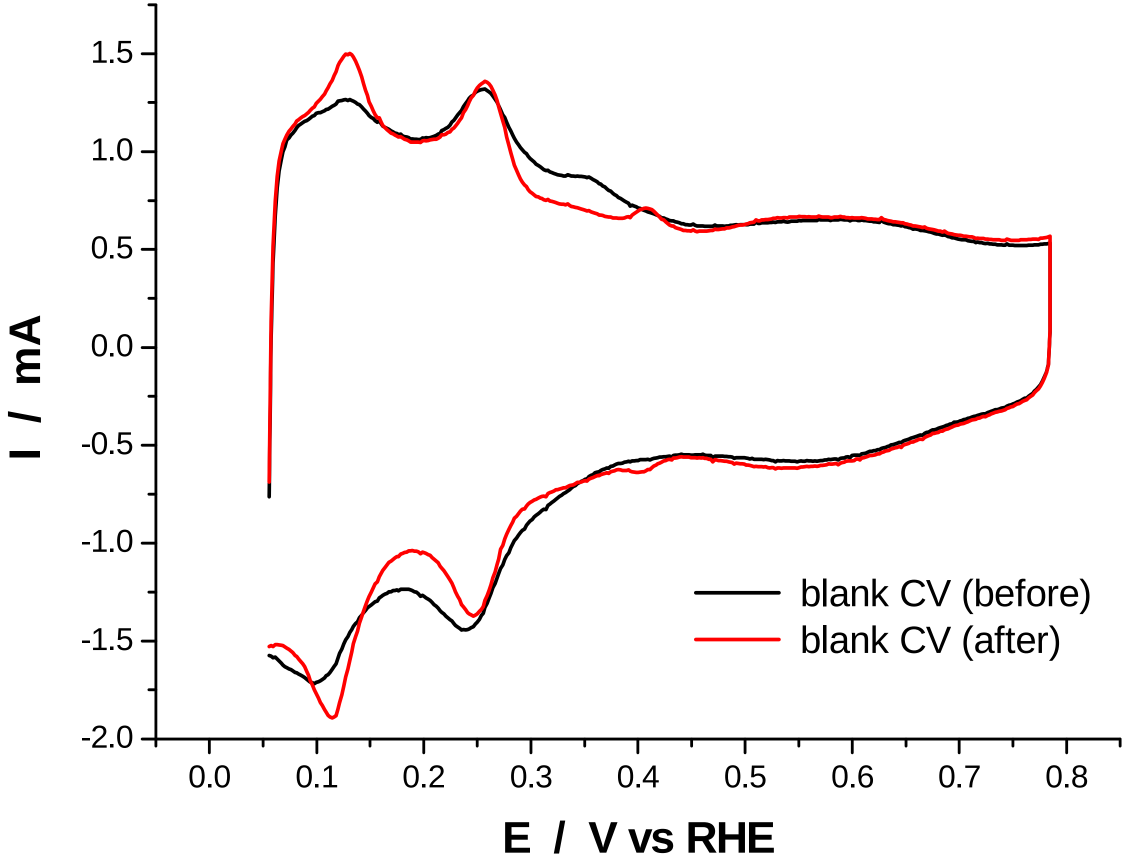
Gradual deactivation of the catalyst is observed

Steady-state resembles Pt

What happens?

$PtWO_3/C$ deactivation during continuous CO oxidation
0.5 M H_2SO_4; 2 mV/s

Continuous CO oxidation



Bronze peak disappears

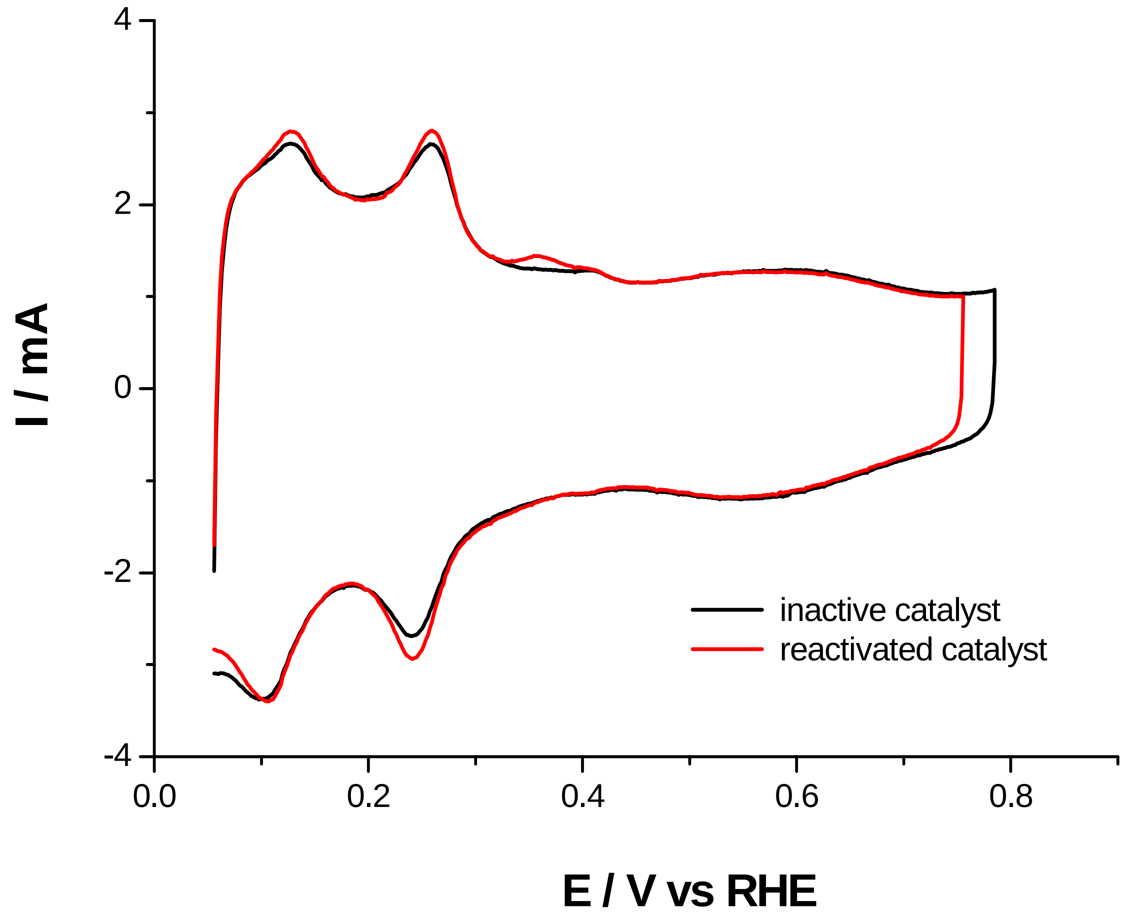
Dissolution WO_3 ?

Deactivation ?

$PtWO_3/C$: blank CVs before and after continuous CO oxidation

0.5 M H_2SO_4; 10 mV/s

Continuous CO oxidation



After exposure to hydrogen evolution conditions
Bronze peak re-appears

No dissolution of WO_3 @ RT

(Reversible) deactivation !

$PtWO_3/C$ catalyst reactivation
(20 min. @ -0.05 V)

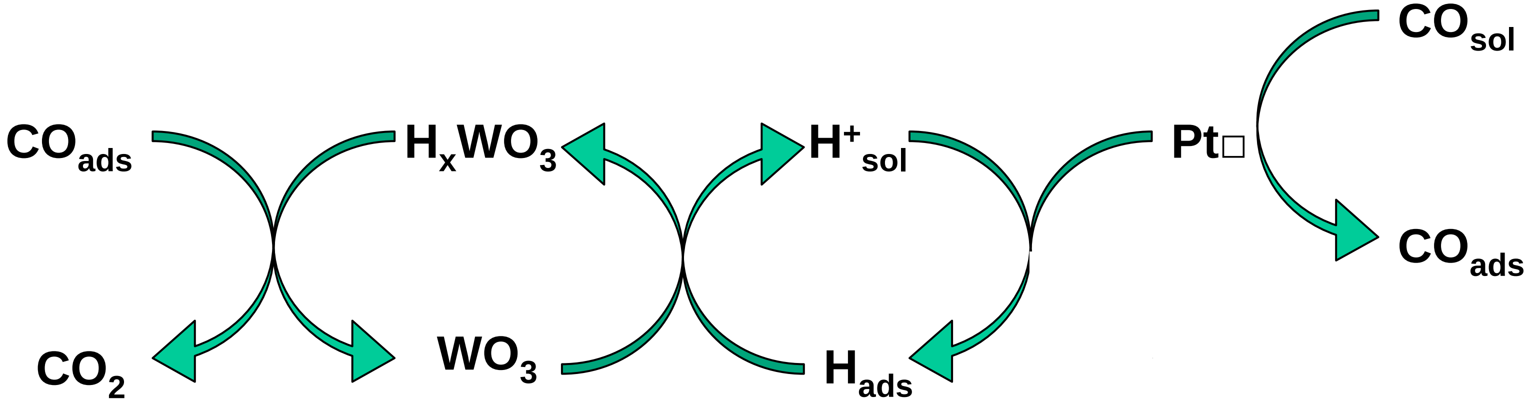
0.5 M H_2SO_4, 20 mV/s

Mechanism of the CO oxidation

$$\mathrm{Pt} + \mathrm{H}^+ + e \longrightarrow \mathrm{PtH}_{ads}$$

$$x\mathrm{PtH}_{ads} + \mathrm{WO}_3{\cdot}y\mathrm{H}_2\mathrm{O} \longrightarrow \mathrm{Pt} + \mathrm{H}_x\mathrm{WO}_3{\cdot}y\mathrm{H}_2\mathrm{O}$$

$$\mathrm{CO}_{Pt} + \mathrm{OH}_{HxWO3} \longrightarrow \mathrm{CO}_2 + \mathrm{WO}_3 + \mathrm{Pt}$$



CO_{sol}

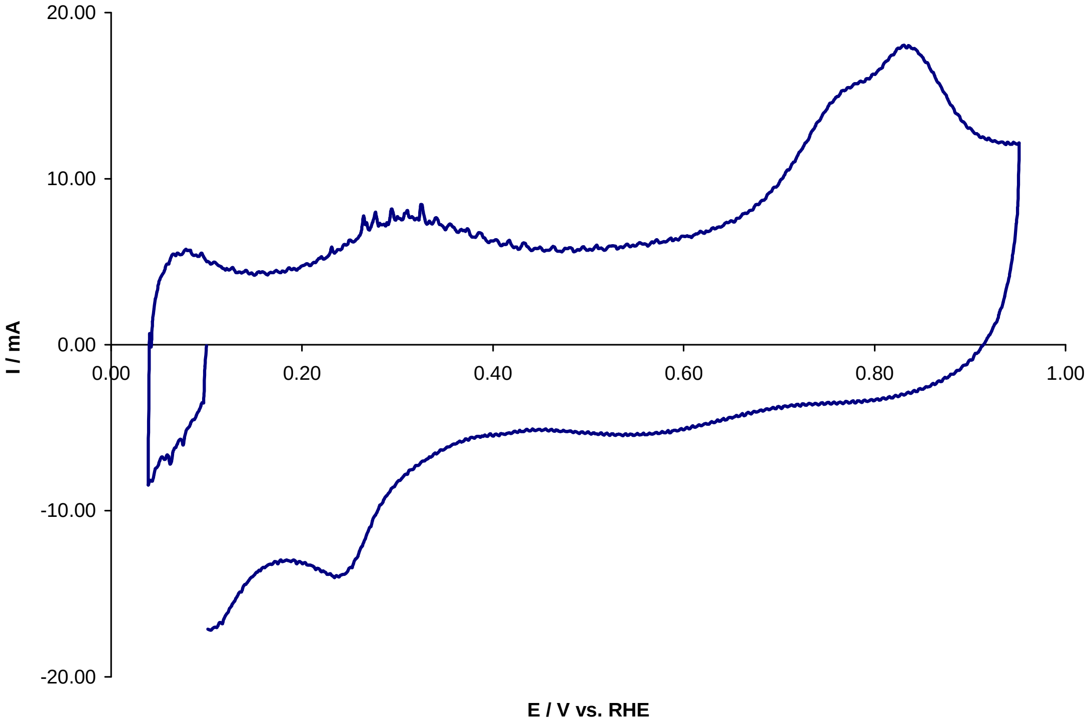
CO_{ads} **H_xWO_3** **H^+_{sol}** **Pt□**

CO_{ads}

CO_2 **WO_3** **H_{ads}**

Where does “O” come from – “lattice” or H_2O – and what is the role of $H_xWO_3{\cdot}yH_2O$?

CO_2 reduction



After exposure to CO_2 – saturated electrolyte an adsorbate forms

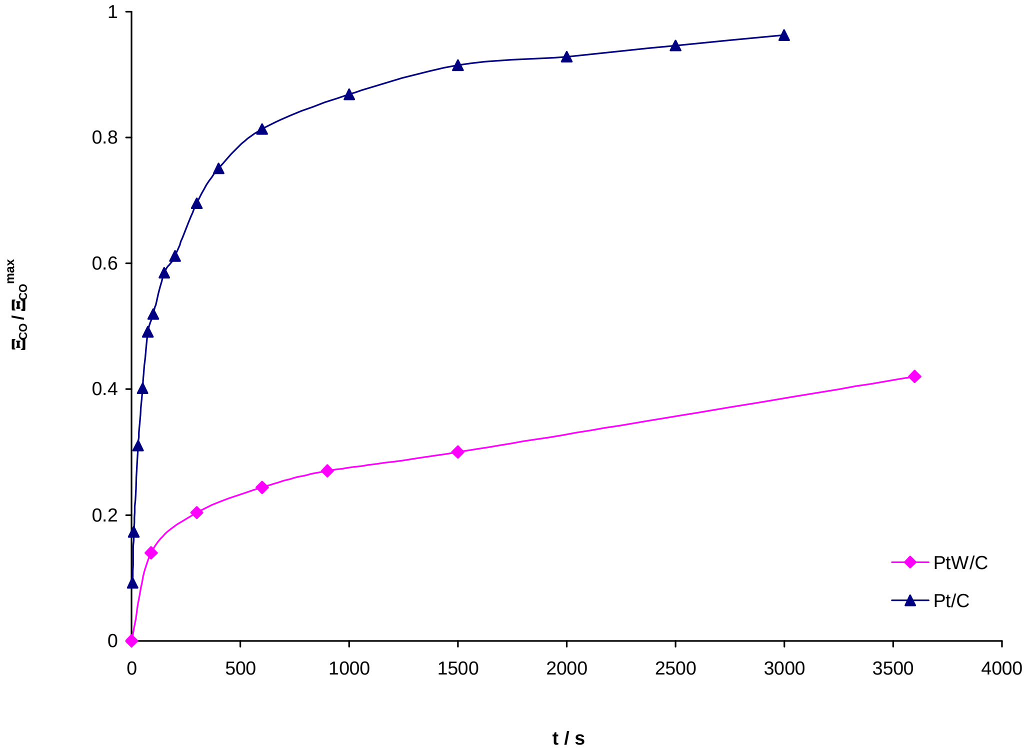
Suppresses Hupd on Pt
Oxidizes similarly to CO

CO

$PtWO_3/C$ catalyst, CO_2 - saturated 0.5 M H_2SO_4, E_{ads} = 0.1 V vs RHE

$$CO_2 + 2H_{ads} \longrightarrow CO + H_2O$$

CO_2 reduction



Rate of the adsorbate formation is much lower on $PtWO_3/C$ than on Pt/C:

- lower Hupd concentration

however

Eventually full coverage will be reached @ RT

$$CO_2 + 2H_{ads} \longrightarrow CO + H_2O$$

Conclusions

- $PtWO_3/C$ is highly active in the oxidation of CO: adlayer begins to oxidize at 0.25 V and dissolved CO at 0.12 V vs. RHE
- H_xWO_3 is the active component & oxygen donor; formation of the bronze is slow in the $PtWO_3/C$ catalyst
- In the presence of CO, the bronze formation (via H spill-over from Pt to WO_3) is inhibited;

  $\Rightarrow$ (reversible) catalyst deactivation.
- $PtWO_3/C$ catalyst reduces CO_2 to CO at much lower rate than Pt/C. Still full coverage is expected at prolonged exposure to CO_2 at RT.
- $PtWO_3/C$ has a limited operating window (ca. 0.10 V to ca. 0.45 V). In case of high overpotential on the anode (start-up, fuel starvation etc.) and/or peak of high CO concentration – possible death of the catalyst.

General recommendations:

- WO_3 phase as crystalline as possible for quick recharging; well dispersed with Pt
- Drying induces ageing $\Rightarrow$ slowing down of recharging $\Rightarrow$ lower catalyst activity

Acknowledgement

Marijke Roos, Energy Research Centre of the Netherlands (ECN), for EDX measurements

Vera Smit-Groen, Nuclear Research and Consultancy Group (NRG), for XRD measurements

Onne Wouters, Nuclear Research and Consultancy Group (NRG), for TEM imaging

Ad Wonders, Eindhoven University of Technology (TUE), for assistance with on-line MS

Tiny Verhoeven, Eindhoven University of Technology (TUE), for XPS measurements