# Pt and Au shell - bimetallic core electrocatalysts through partial electroless replacement of metal (M) deposits by Pt or Au (M: Pb, Cu, Co, Ni)

# Principle of electroless replacement of metals *"transmetalation"*

$$M_{noble}^{n+} + n/m\ M \rightarrow M_{noble} + n/m\ M^{m+}$$

$M_{noble}^{n+} + n\ e^- \leftrightarrow M_{noble}$ $\quad E^0_{noble}$ $\quad E^0_{noble} - E^0 > 0$

$M^{m+} + me^- \leftrightarrow M$ $\quad E^0$

e.g.

$$PtCl_6^{2-} + 2\ M \rightarrow Pt + 2\ M^{2+} + 6\ Cl^-$$

$$2\ AuCl_4^- + 3M \rightarrow 2\ Au + 3\ M^{2+} + 8\ Cl^-$$

M: Pb, Cu, Co, Ni

$PtCl_6^{2-} + 4e^- \leftrightarrow Pt + 6Cl^-$ $\quad E^0 = +0.744$ V

$AuCl_4^- + 3e^- \leftrightarrow Au + 4Cl^-$ $\quad E^0 = +1.002$ V

$Cu^{2+} + 2e^- \leftrightarrow Cu$ $\quad E^0 = +0.340$ V

$Pb^{2+} + 2e^- \leftrightarrow Pb$ $\quad E^0 = -0.126$ V

$Ni^{2+} + 2e^- \leftrightarrow Ni$ $\quad E^0 = -0.257$ V

$Co^{2+} + 2e^- \leftrightarrow Co$ $\quad E^0 = -0.277$ V

favourable exchange

# Characteristics of the presented method variant

➢ Thick electrodeposits of M (Pb, Cu, Co, Ni) are electrodeposited (equivalent of 300-1500 flat ML) on glassy carbon (GC) substrates:

- avoid complete M dissolution; ensure good GC coverage
- form Pt or Au-shell M-containing-core particles

  (use the method for catalysts with non-noble/noble metal interactions)
- tune the composition of the Pt-M, Au-M bi-metallic catalysts.

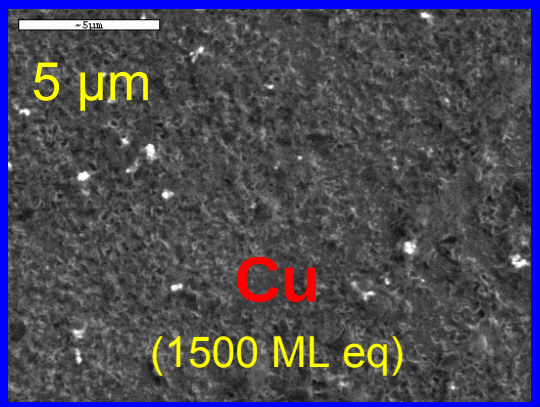
➢ Electrochemical treatment (positive potentials):

- ensure that only particles with defect-free Pt or Au shells remain

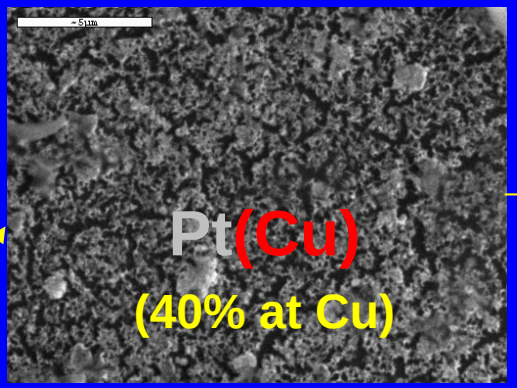
➢ Room temperature during all process steps (no annealing):

- skip energy and labour intensive step
- study of interactions of the non-alloyed Pt-M core to the Pt shell

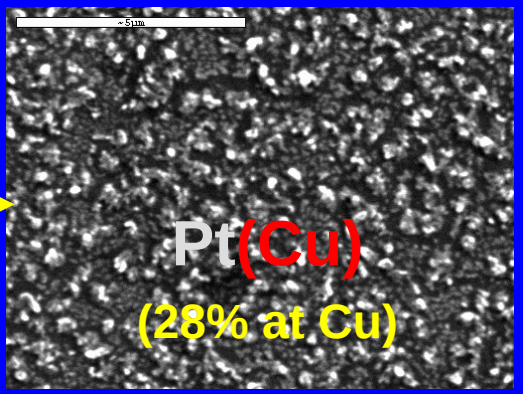
# SEM and EDS of indicative M, Pt(M) and Au(M) deposits

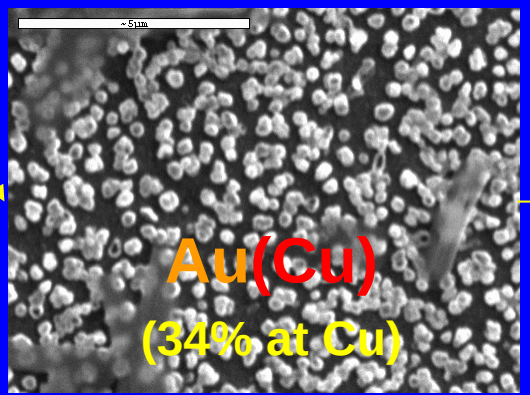


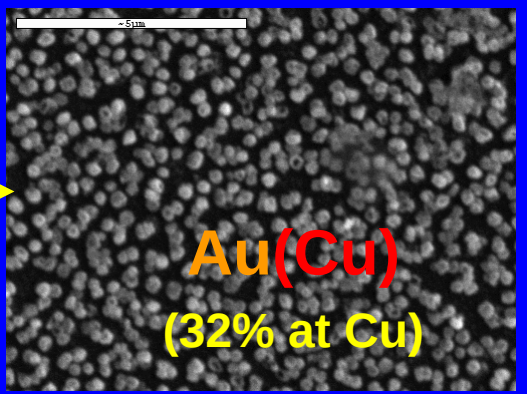

exchange




activation

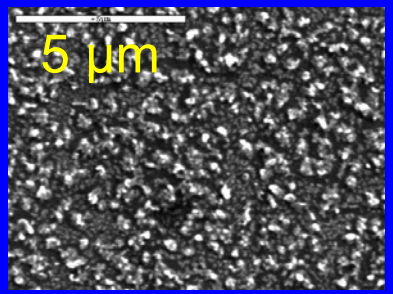


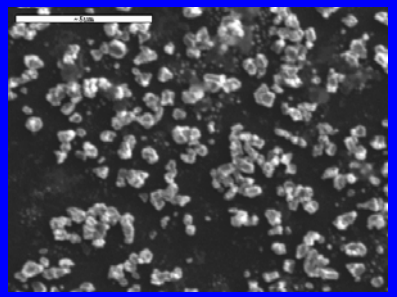



# SEMs of M, Pt(M) and Au(M) tested

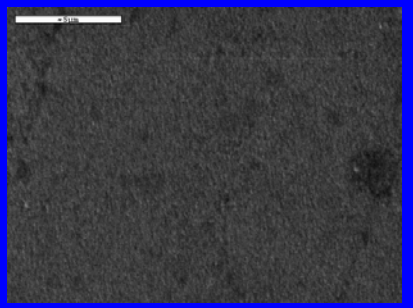
**Pt(Cu 28%)**
(from1500 ML)



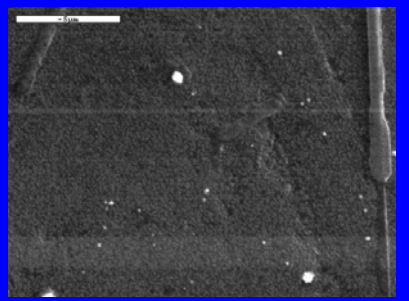

**Pt(Pb 27%)**
(from1000 ML)

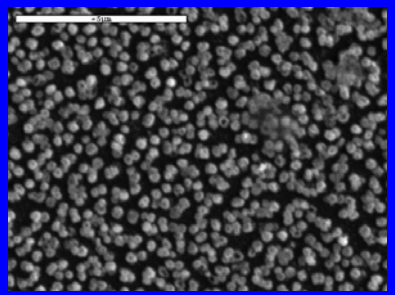


**Pt(Ni 23%)**
(from 300 ML)

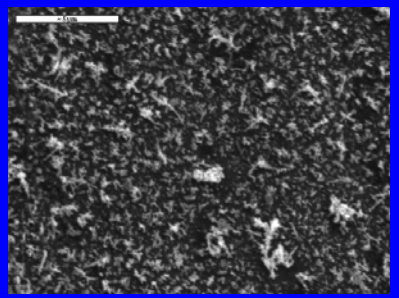


**Pt(Co 27%)**
(from 300 ML)

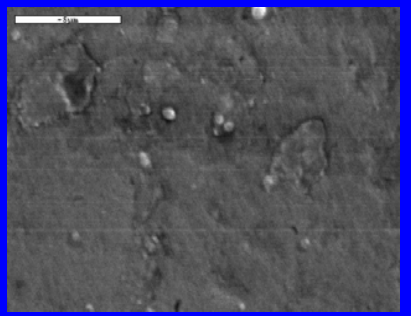




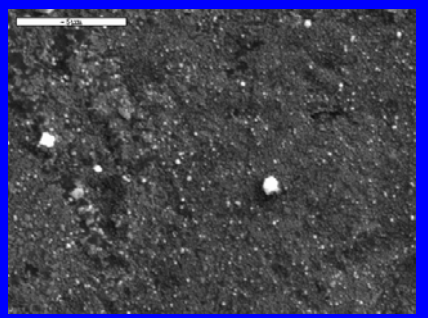
**Au(Cu 32%)**
(from1500 ML)



**Au(Pb 20%)**
(from1000 ML)



**Au (Ni 5%)**
(from 300 ML)



**Au (Co 4%)**
(from 300 ML)

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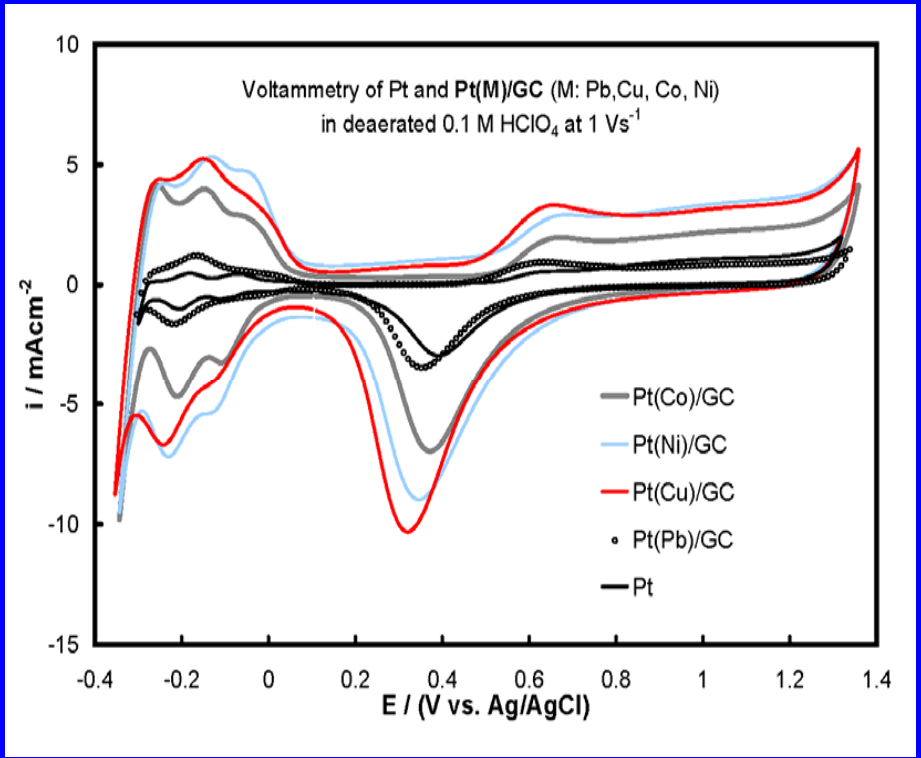
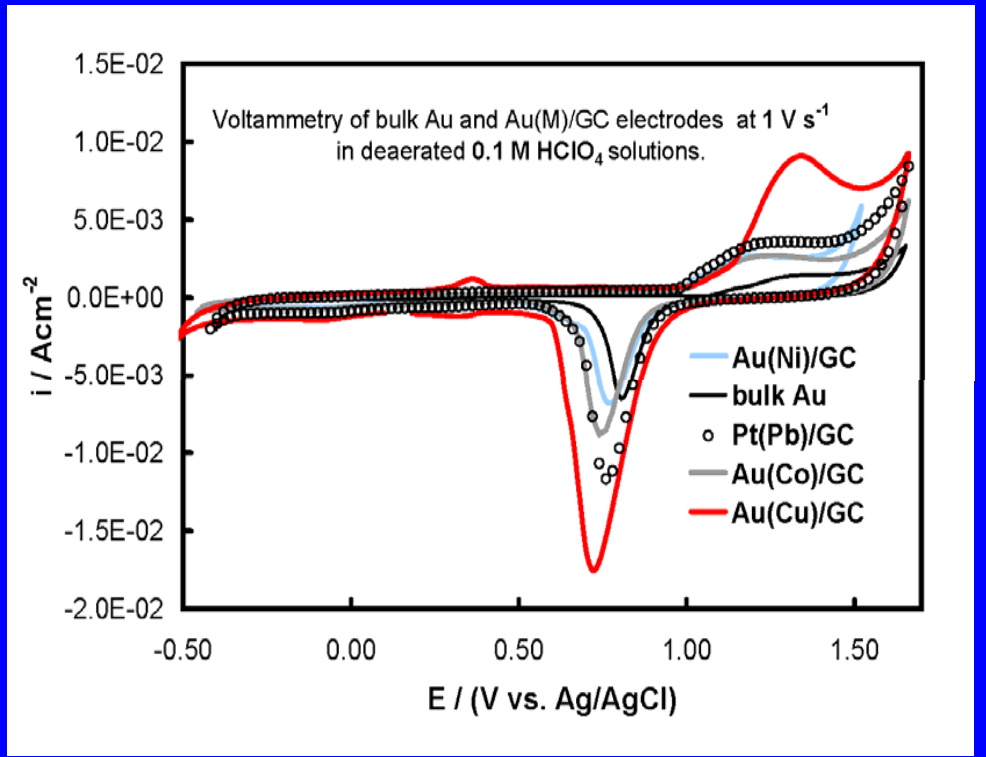
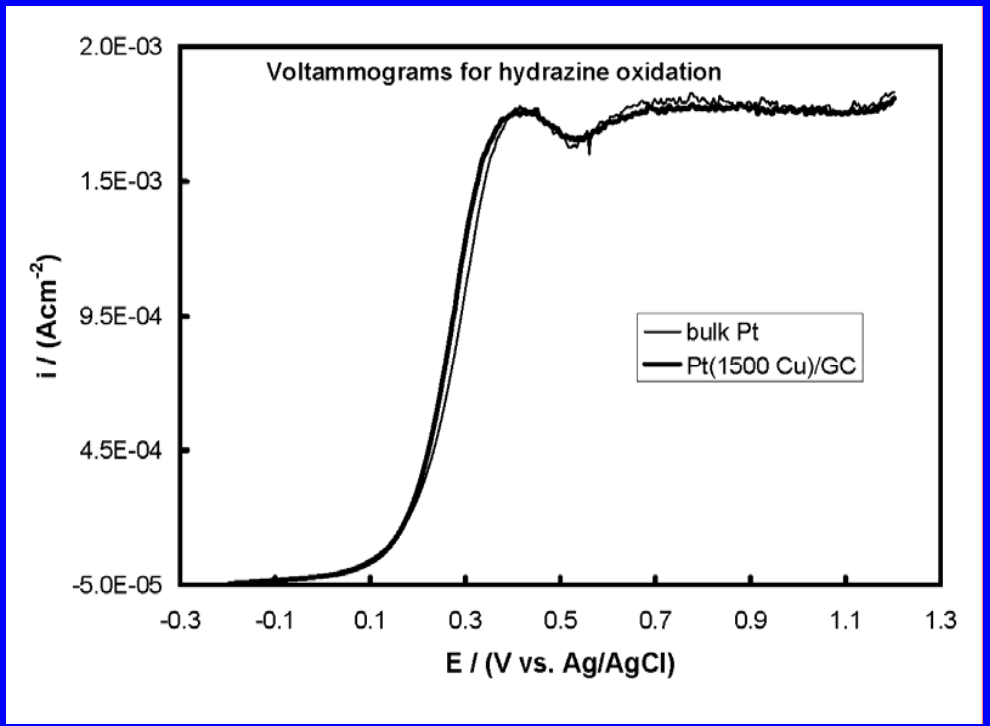
# Electrochemical characterisation-I



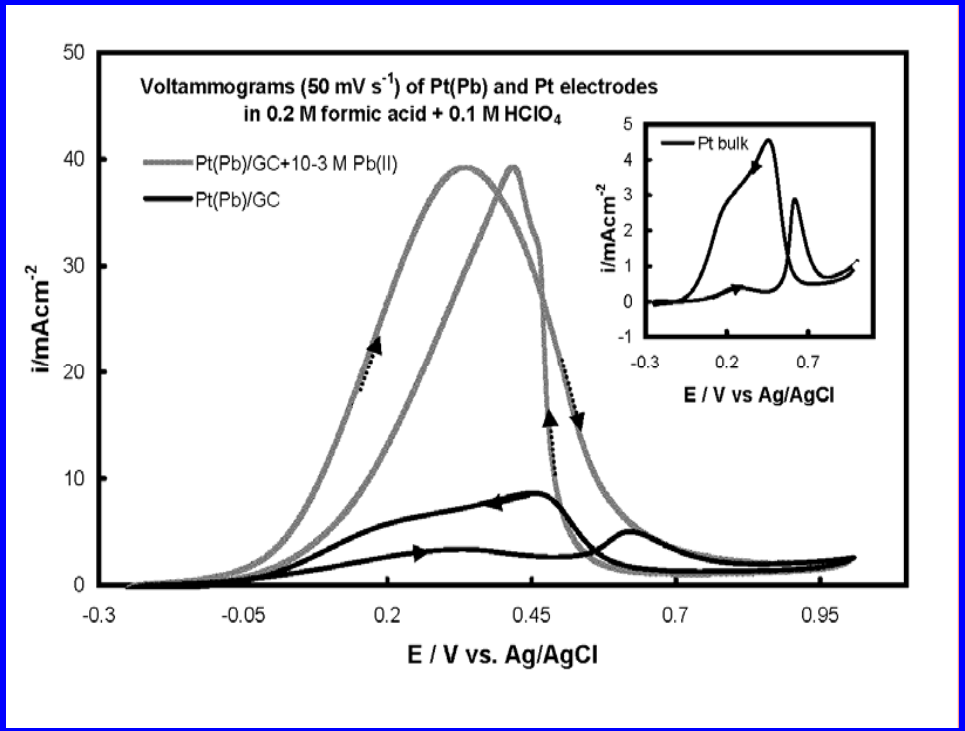




- Surface electrochemistry same as of bulk Pt and Au: only Pt or Au on the surface
- Electroactive surface areas: 2-8 - fold increase from geometric area

# Electrochemical characterisation-II




Hydrazine oxidation on Pt(Cu)




Formic acid oxidation on Pt(Pb)

- Cu UPD would hinder hydrazine oxidation: Cu does not re-deposit from the core to the Pt shell
- Pb UPD would catalyze formic oxidation: Pb does not re-deposit from the core to the Pt shell

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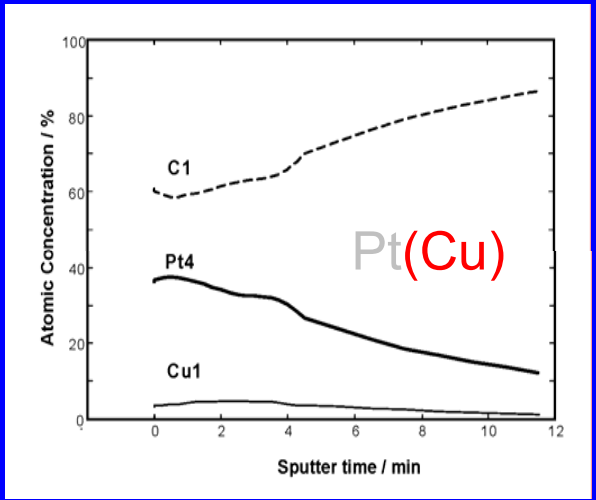
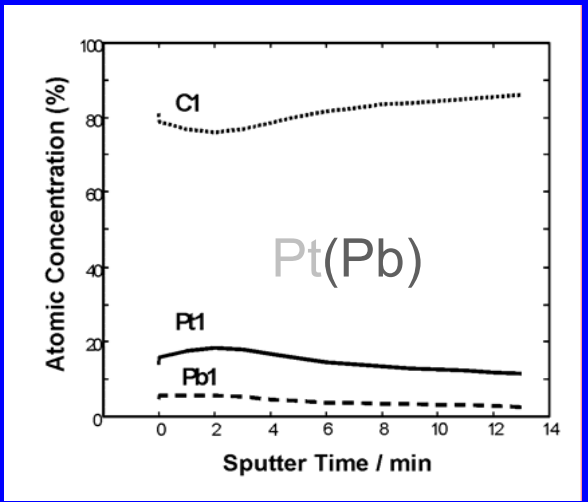
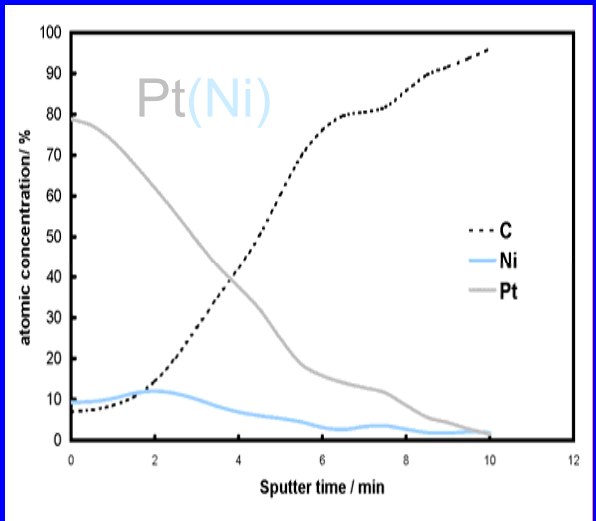
# *Pt and Au shell - bimetallic core (Pt-M, Au-M) electrocatalysts*

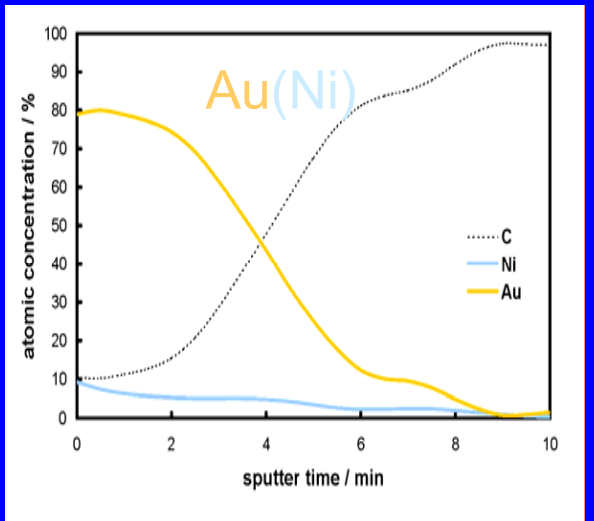
## Sputter-etch AES characterisation




- M signal before sputter:
  2-4 ML thick Pt or Au shell
- Pt, Au signals down to the substrate:
  Pt-M or Au-M core
- High C signal (from substrate):
  sparse or uneven thickness deposits




## XRD characterisation

- no alloy formation

in Pt- M and Au-M core

*(~S.Wang et al, Appl.Surf.Sci. 254 (2008) 2102)*

- Pt crystallite size: 7-11 nm
  Au crystallite size: 10-15 nm

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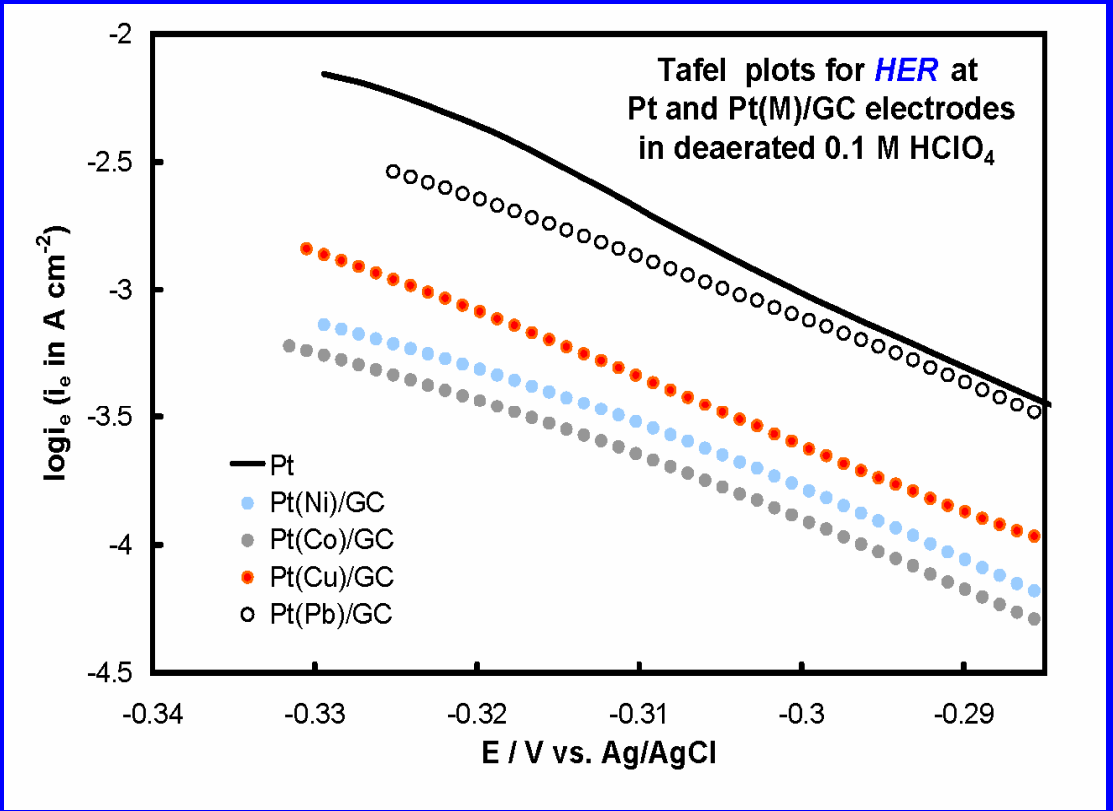
# Hydrogen evolution reaction (*HER*)




- suppression of HER at Pt(Co), Pt(Ni) and Pt(Cu):

**weakening** of the Pt(M)-$H_{ads}$ bond strength

~ d-band center ($\varepsilon_d$) lowering due to strain and ligand effects

*(DFT predictions by Nørskov and co-workers; experimental evidence)*

~ hydrogen binding energy trends

*(DFT predictions by Mavrikakis and co-workers)*

candidates for **hydrogenation reactions**

(intermediate M-H bond strength)

- unaffected HER at Pt(Pb):

no DFT predictions; lower Wegner-Scheizer radius but higher Pauling electronegativity

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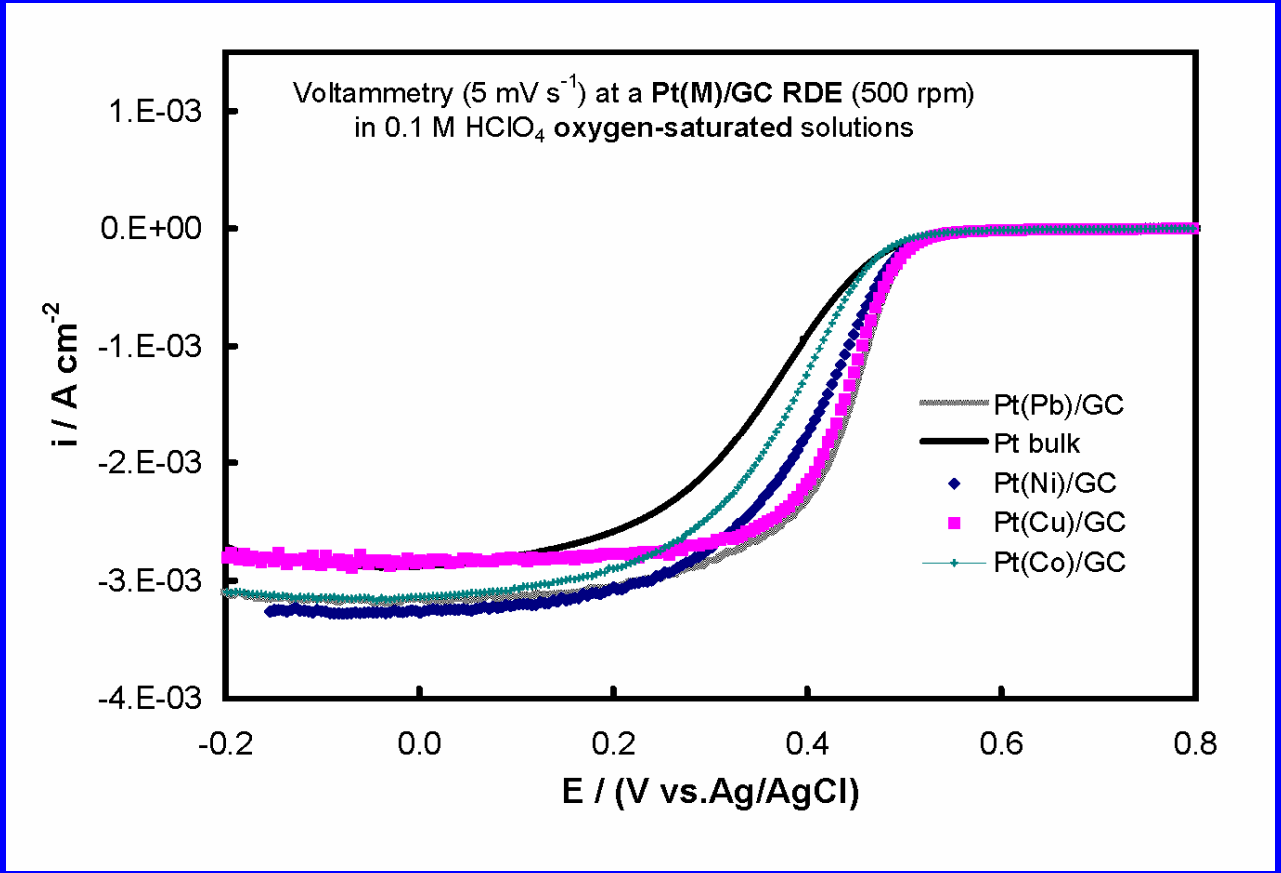
# Oxygen reduction reaction (*ORR*)



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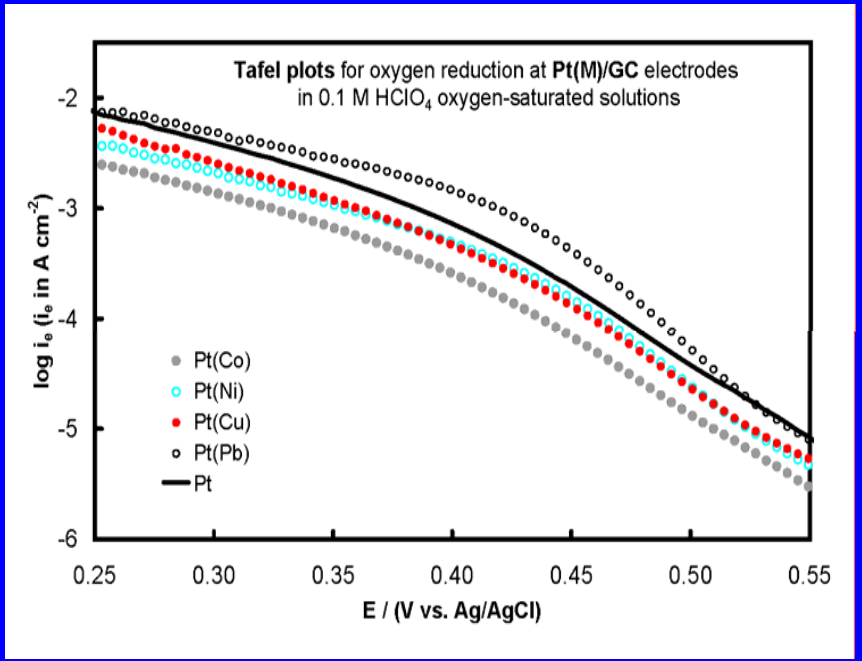
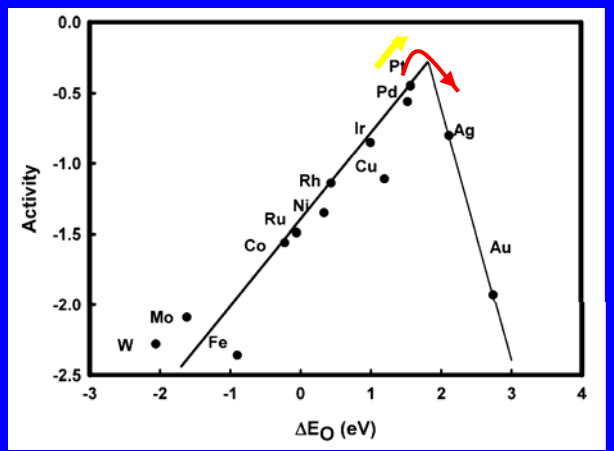



- slight suppression of ORR at Pt(Co), Pt(Ni) and Pt(Cu):

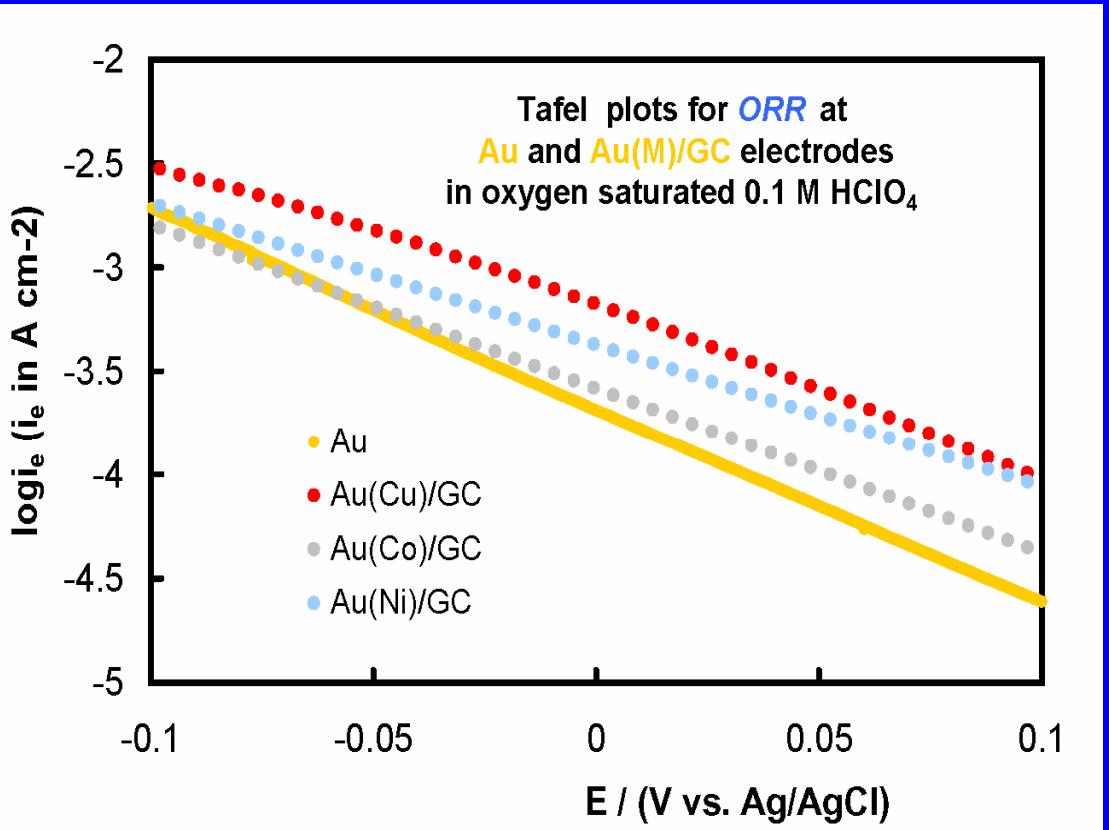
  ≠ *extensive literature on similar Pt-shell/$Pt_3M$* ***alloy*** *catalysts (both experimental and DFT results)*

  **large** $\varepsilon_d$ down-shift due to larger ligand and strain effects by **non-alloyed M** regions in the core

Further decrease of Pt-O bond strength (increase in $\Delta E_O$)but also of dissociative $O_2$ adsorption



# Oxygen reduction reaction (*ORR*)



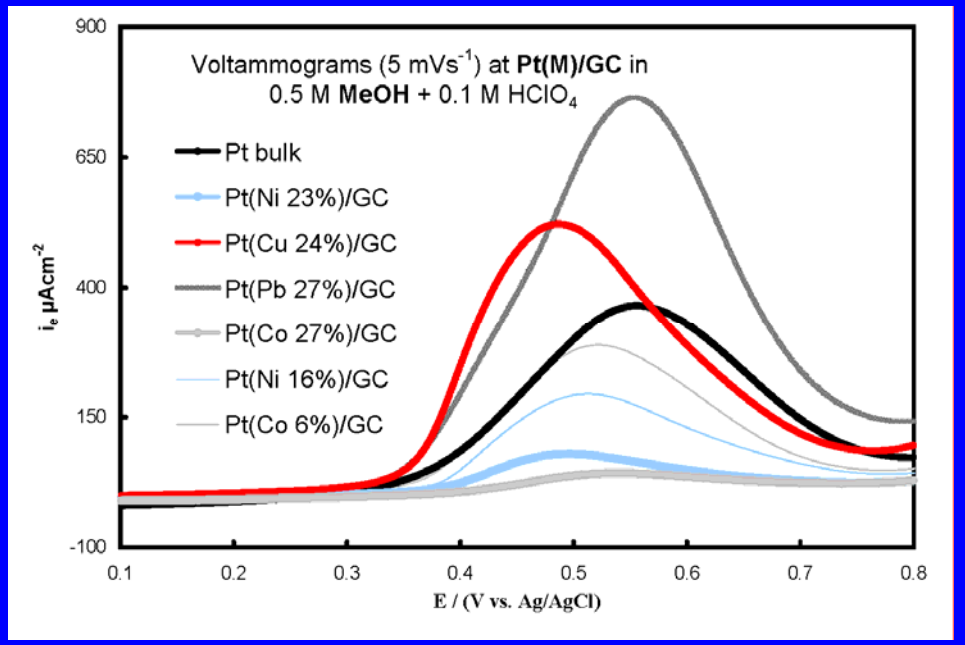

- enhancement of ORR at Au(Cu), Au(Ni) and Au(Co):

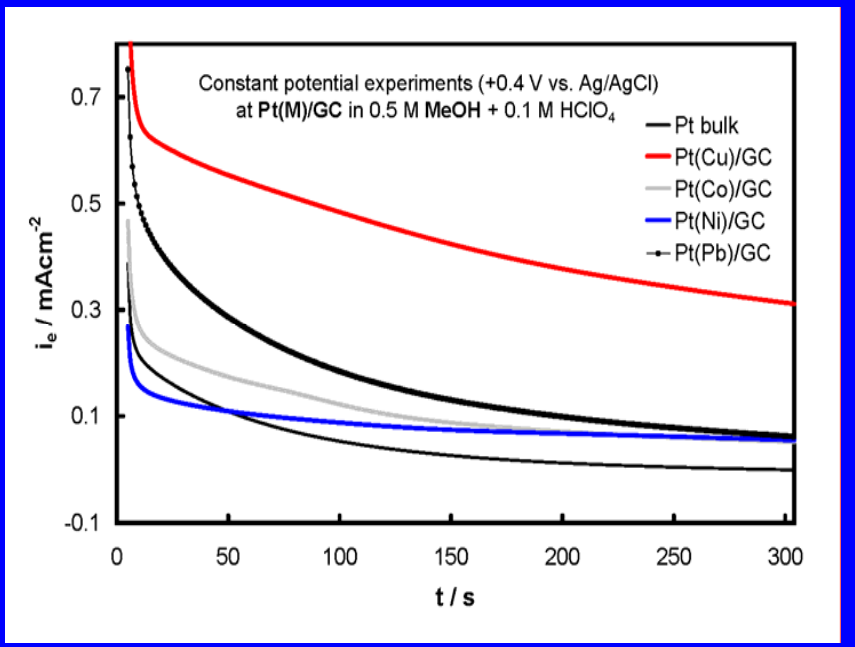
-difference in ORR mechanism

-no oxides present

-extraordinary properties (increased molecular oxygen adsorption) of very small particles or very thin films of Au

# Methanol oxidation reaction (*MOR*)




- enhancement of MOR at Pt(Cu), Pt(Pb)
- decrease at Pt(Ni), Pt(Co)

(≠literature for alloys)

- enhancement of MOR short term stability at Pt(Cu), Pt(Pb), Pt(Ni), Pt(Co)

(~literature for tolerance to CO poisoning)

Interplay between CO poisoning and MeOH chemisorption

Pt(Cu) : moderate $\varepsilon_d$ downshift and adsorption affinity →best performance

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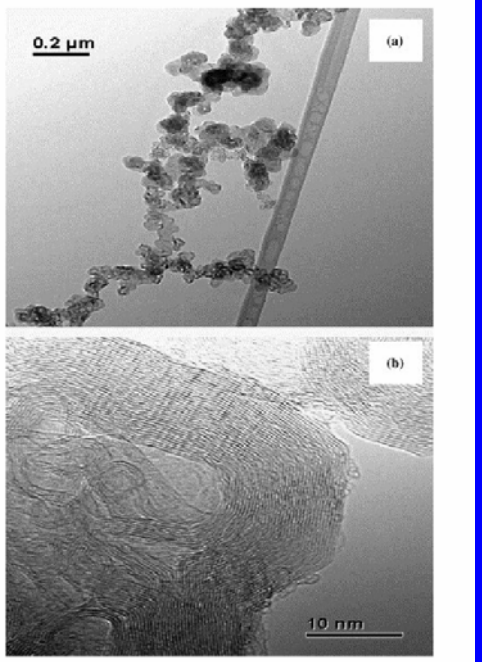
# Towards the application of the method to practical catalysts




Pure Black Carbon (PB)

(Barsukov and co-workers)

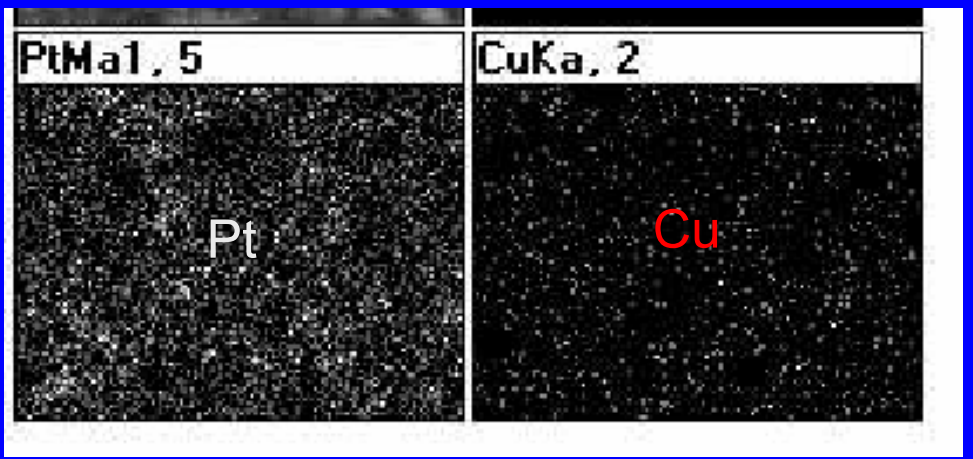
Impregnation

$H_2$ annealing

30% Cu/PB → Pt(Cu 50%)/PB

+Nafion

Pt(Cu 50%)/PB/GC

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