Pt-M AND Au-M BIMETALLIC ELECTROCATALYSTS (M = Pb, Cu, Fe, Co, Ni) PREPARED BY A GALVANIC REPLACEMENT PROCESS

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FUEL CELL ELECTROCATALYSIS

Improvement of the catalytic activity of Pt for fuel cell electrocatalysis.

❒ ***Modification with ad-atoms – Modes of action***

1) The third-body mechanism
2) The prevention of poison formation
3) The bifunctional mechanism
4) The modification of the electronic properties of the electrode surface.

❒ ***Increase the catalyst utilization***

Dispersion of micro- and nano-structured metal particles on porous materials.

↗ Electrocrystallization

↗ Electroless deposition

‰ Two-step Procedure (electrodeposition of non-precious metal and electroless replacement by a precious metal)

ELECTROLESS DEPOSITION OF Pt ON Ti

Immersion of Ti in an aqueous 0.1 M $HClO_4$ solution containing $2x10^{-3}$ M K_2PtCl_6

$$Ti(bulk) + PtCl_6^{-2} \rightarrow Pt^0/Ti + Ti^{IV} + 6Cl^-$$

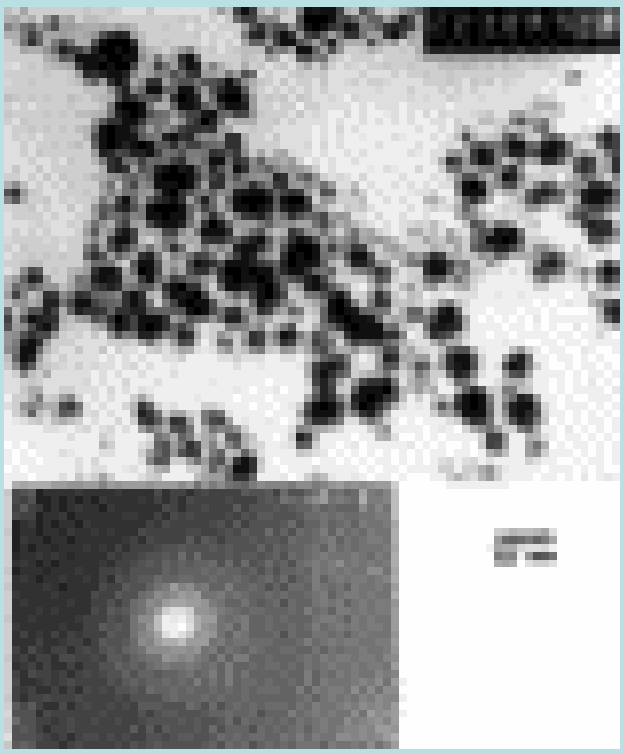


Fig. 2. TEM image and the corresponding diffraction pattern of electroless deposited Pt crystals on freshly polished Ti after immersing it in 0.1 M $HClO_4$ + $2x10^{-3}$ M K_2PtCl_6 solution for 60 s.

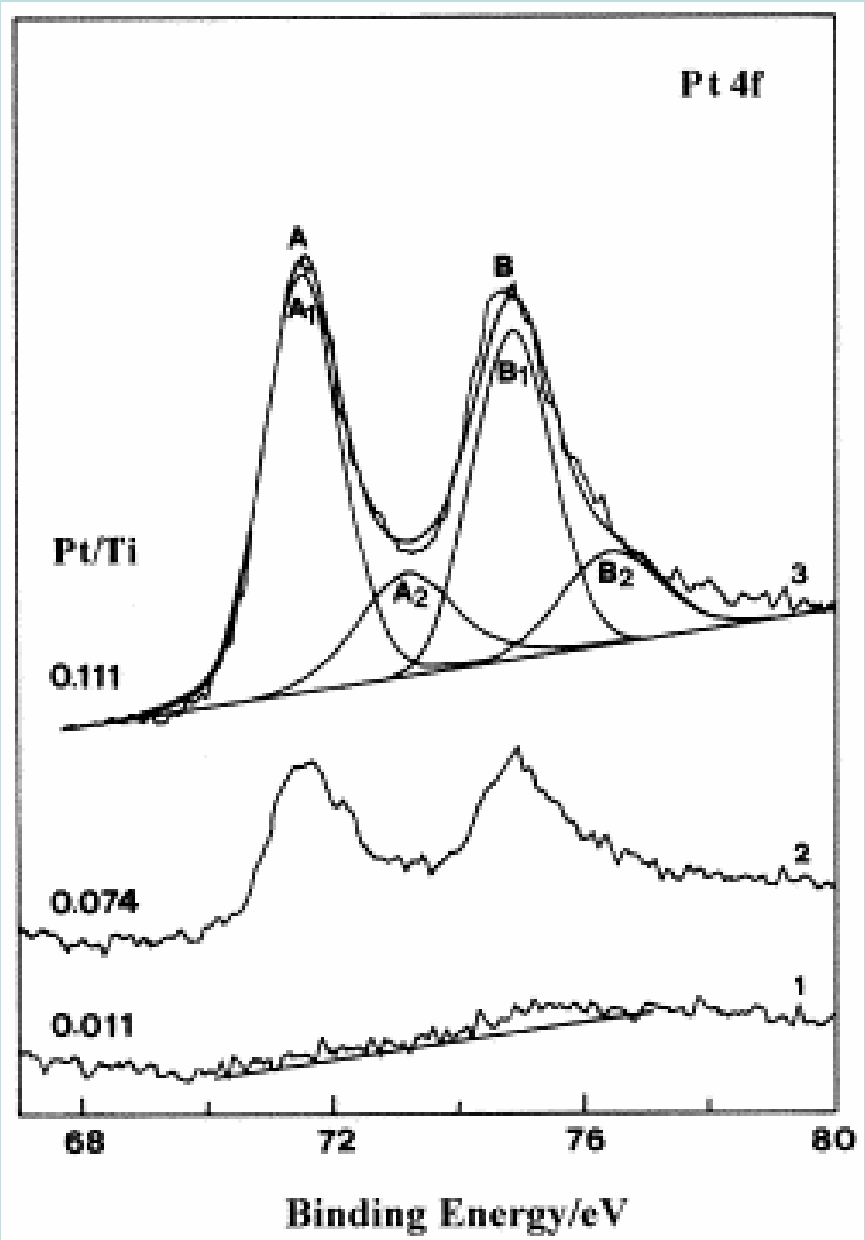


Fig. 3. XPS spectra for Pt 4f obtained from Pt/Ti samples prepared by immersing a freshly polished Ti plate in 0.1 M $HClO_4$+2×10^{-4} M K_2PtCl_6 solution for: (1) 5 s; (2) 10 s; (3) 60 s. A and B: original platinum peaks; A1 and B1: deconvoluted platinum peaks; A2 and B2: deconvoluted pltainum oxide (PtO) peaks.

HYDROGEN EVOLUTION ON Pt/Ti ELECTRODES

Cyclic voltammogram of the Pt/Ti electrode in 0.1 M $HClO_4$ and the *I*(E) quasi-stationary polarization curve for the HER in the same solution.

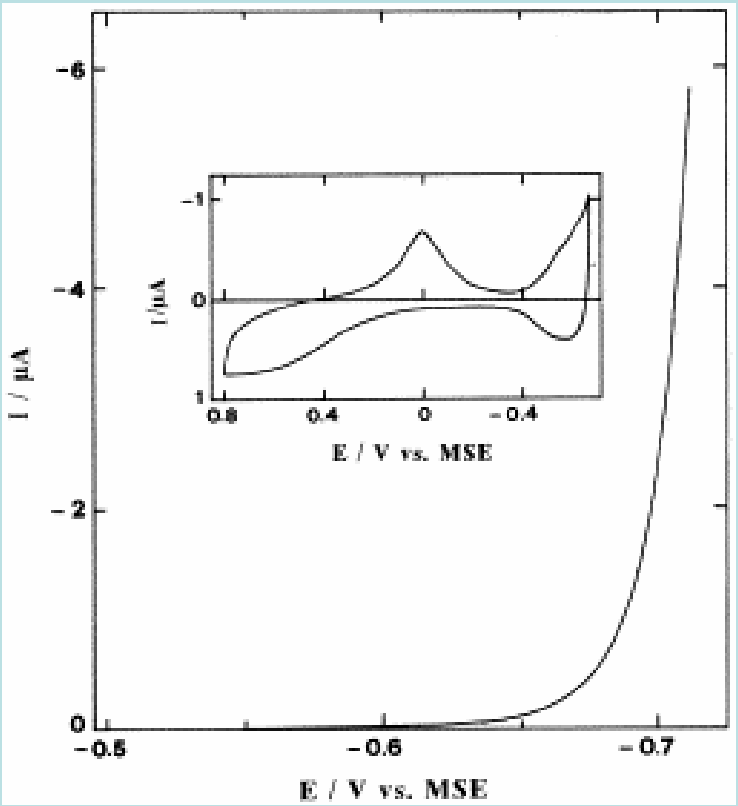


Fig. 4. Quasi stationary *I*(*E*) voltammogram for the HER on Pt(t_d = 10 s)/Ti in aqueous 0.1 M $HClO_4$ solution. dE/dt = 5 mV s^{-1}.

The inset shows the cyclic voltammogram of the Pt/Ti electrode in 0.1 M $HClO_4$ (v = 50 mV s^{-1}).

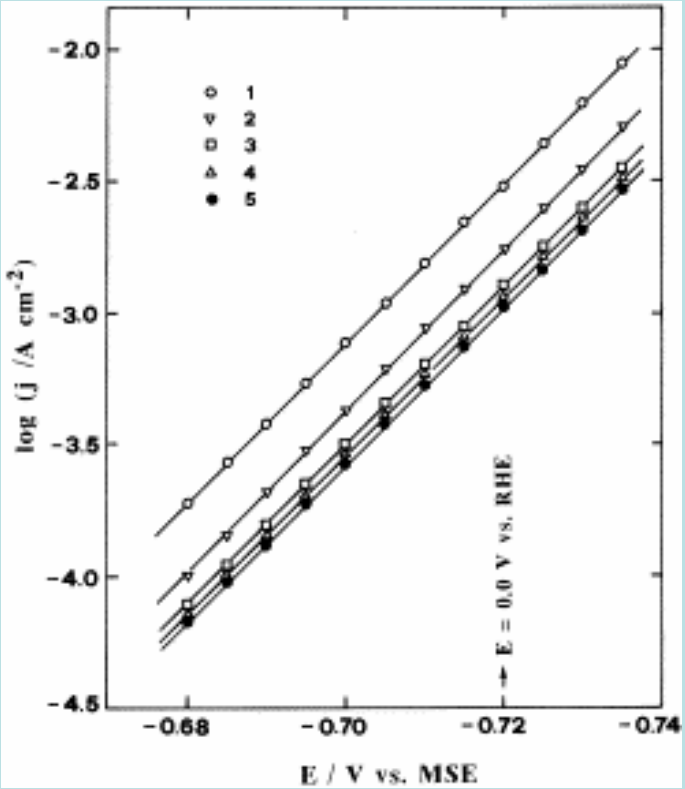


Fig. 5. Tafel plots for HER on Pt/Ti and smooth Pt electrodes in aqueous 0.1 M $HClO_4$ solution.

(1) Pt (t_d = 2 s)/Ti
(2) Pt (t_d = 4 s)/Ti
(3) Pt (t_d = 10 s)/Ti
(4) Pt (t_d = 60 s)/Ti
(5) Smooth Pt.

Note

The smaller the platinum particles the higher the catalytic activity is

OXYGEN REDUCTION ON Pt/Ti ELECTRODES

The next system studied was the reduction of oxygen on Ti covered by electroless-deposited Pt in 0.1 M $HClO_4$ aqueous solution.

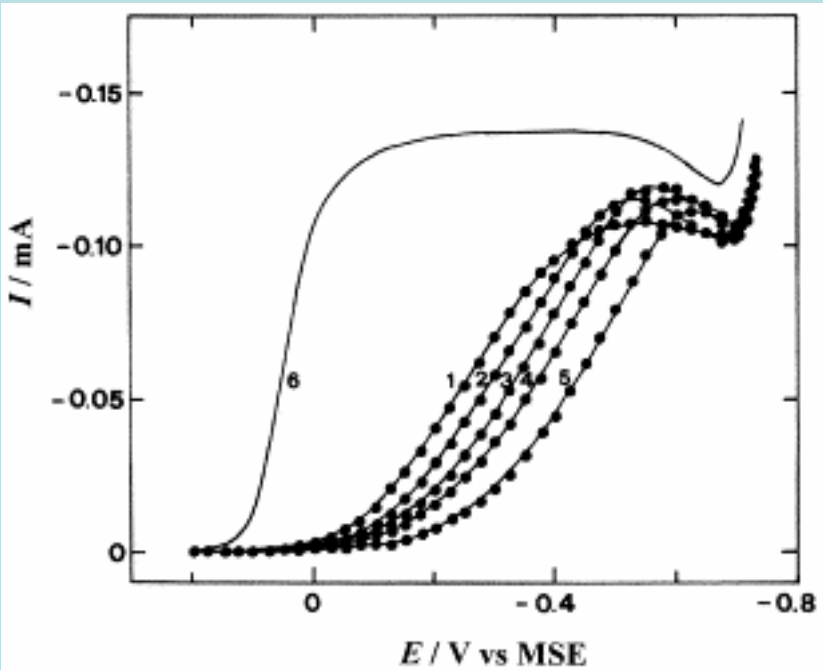


Fig. 6. Averaged current–potential curves for oxygen reduction on a Pt/Ti rotating-disc electrode in O_2-saturated 0.1 M $HClO_4$ (dE/dt = 20 mV s^{-1}). Rotation frequency f = 18.33 Hz.

(1) Pt(t_d = 5 s)/Ti
(2) Pt(t_d = 15 s)/Ti
(3) Pt(t_d = 20 s)/Ti
(4) Pt(t_d = 35 s)/Ti
(5) Pt(t_d = 60 s)/Ti
(5) Smooth Pt

GOLD SUPPORTED Pt ELECTROCATALYSTS FOR O_2 REDUCTION

Two-step procedure:

- Deposition of a less n oble metal (*i.e* Cu, Pb etc.) electrochemically
- Deplacement by platinum at open-circuit potential

$$2Cu^0/Au + PtCl_6^{-2} \rightarrow Pt^0/Au + 2Cu^{2+} + 6Cl^-$$

- The time of copper deposition was changed from 3 s to 120 s
- The displacement time with Pt was kept constant equal to 180 s.

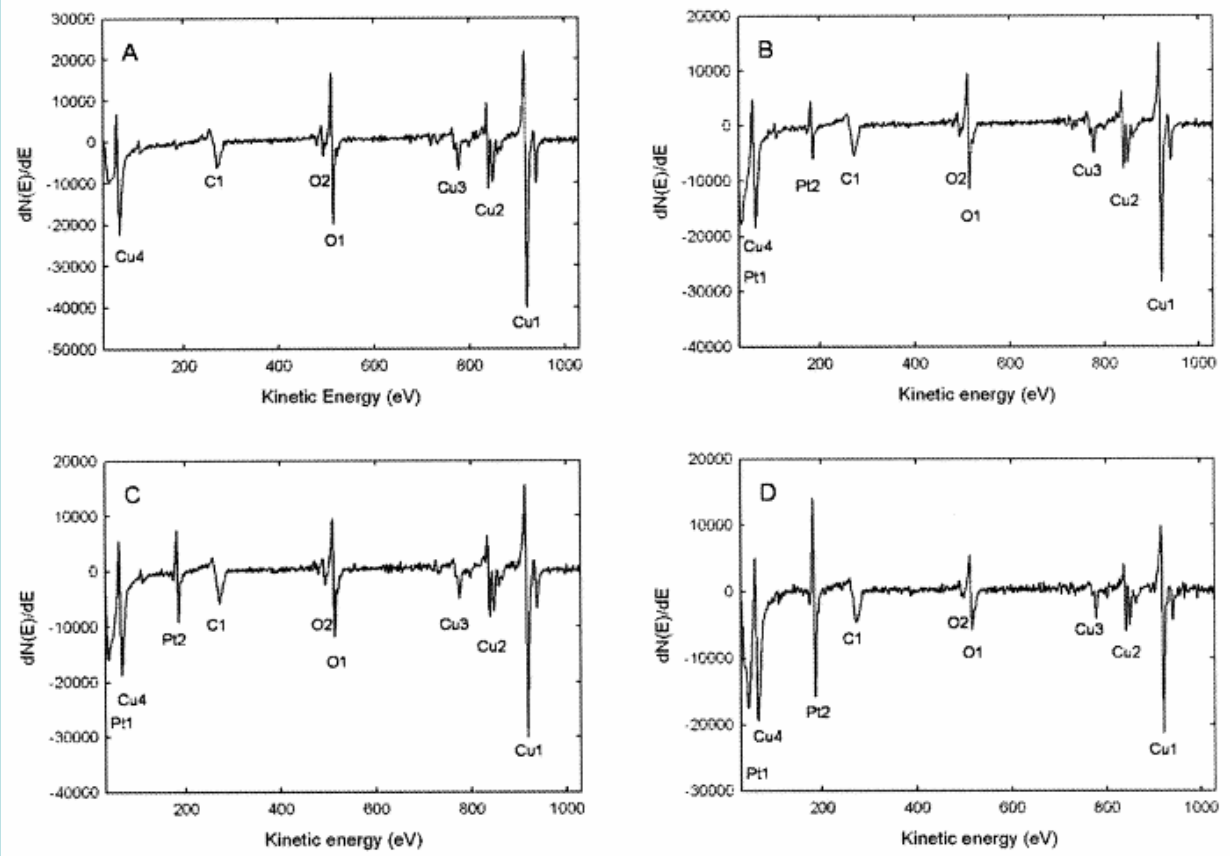


Fig. 8. AES spectra for the system Pt/(Cu_{60s})/Au at different immersion times. (A) 0 s; (B) 60 s; (C) 120 s; (D) 180 s.

Note

Even at immersion time of 180 s the Cu amount was not fully displaced by Pt

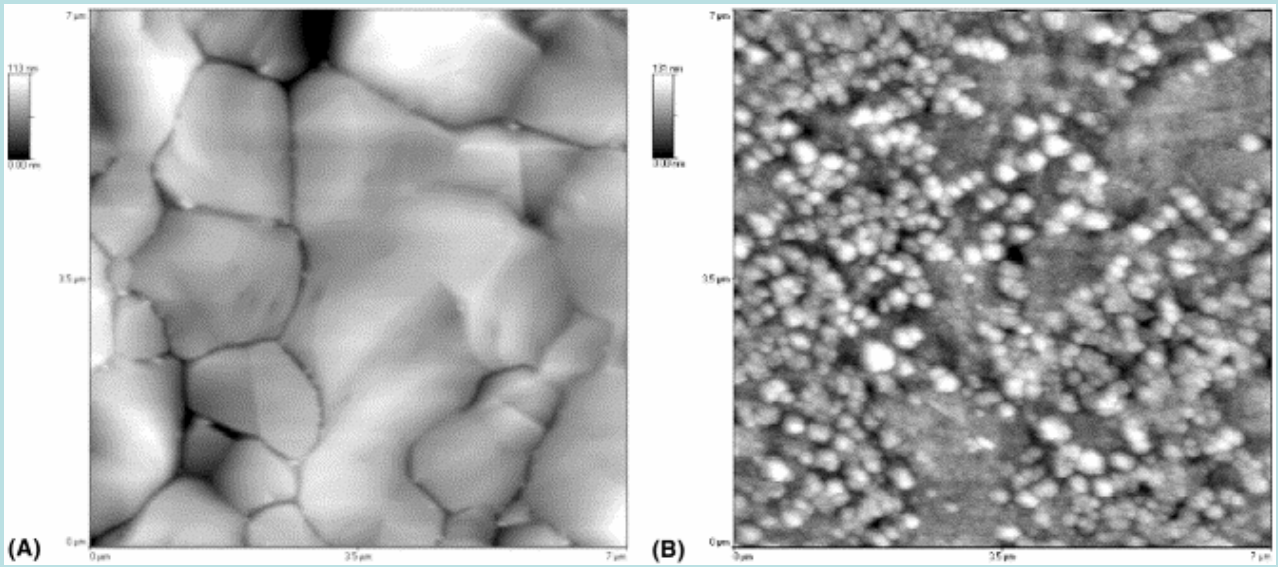


Fig. 9. AFM contact mode images of (A) bare Au and (B) Au covered by Pt deposit.

$t_{Cu,\ dep}$ = 60 s

$t_{Pt,\ repl}$ = 180 s

- The metallic particles are almost uniformly spread on the Au substrate.
- The size of the particles is about 50 – 100 nm in diameter and consists of agglomerated crystallites of much smaller dimensions.

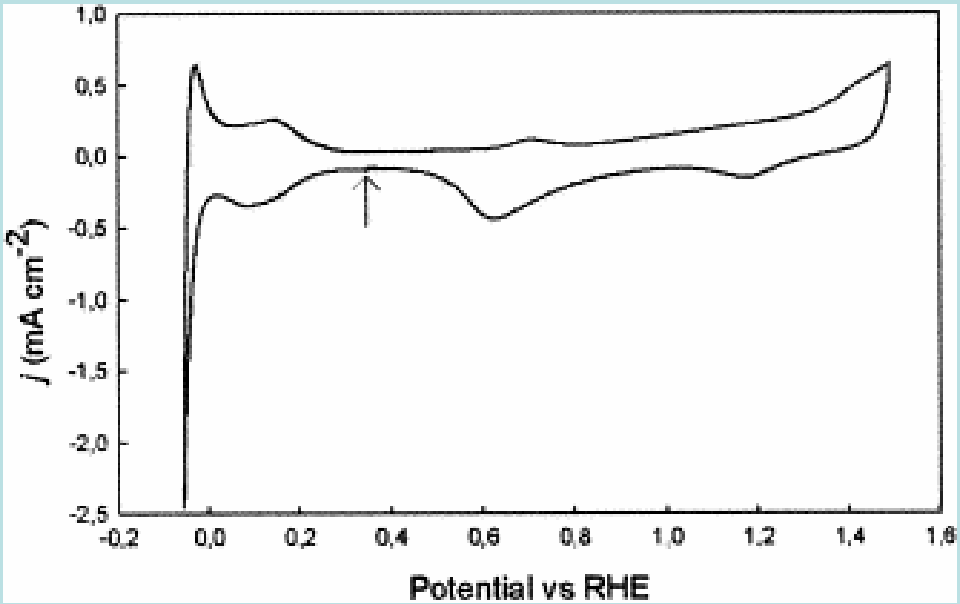


Fig. 10. Cyclic voltammogram of a Pt(Cu)/Au modified electrode in oxygen-free 0.1 M $HClO_4$ (dE/dt = 50 mV s^{-1}).

$t_{Cu,\ dep}$ = 60 s

$t_{Pt,\ repl}$ = 180 s

➔ The cyclic voltammogram shows typical features for both polycrystalline gold and platinum.

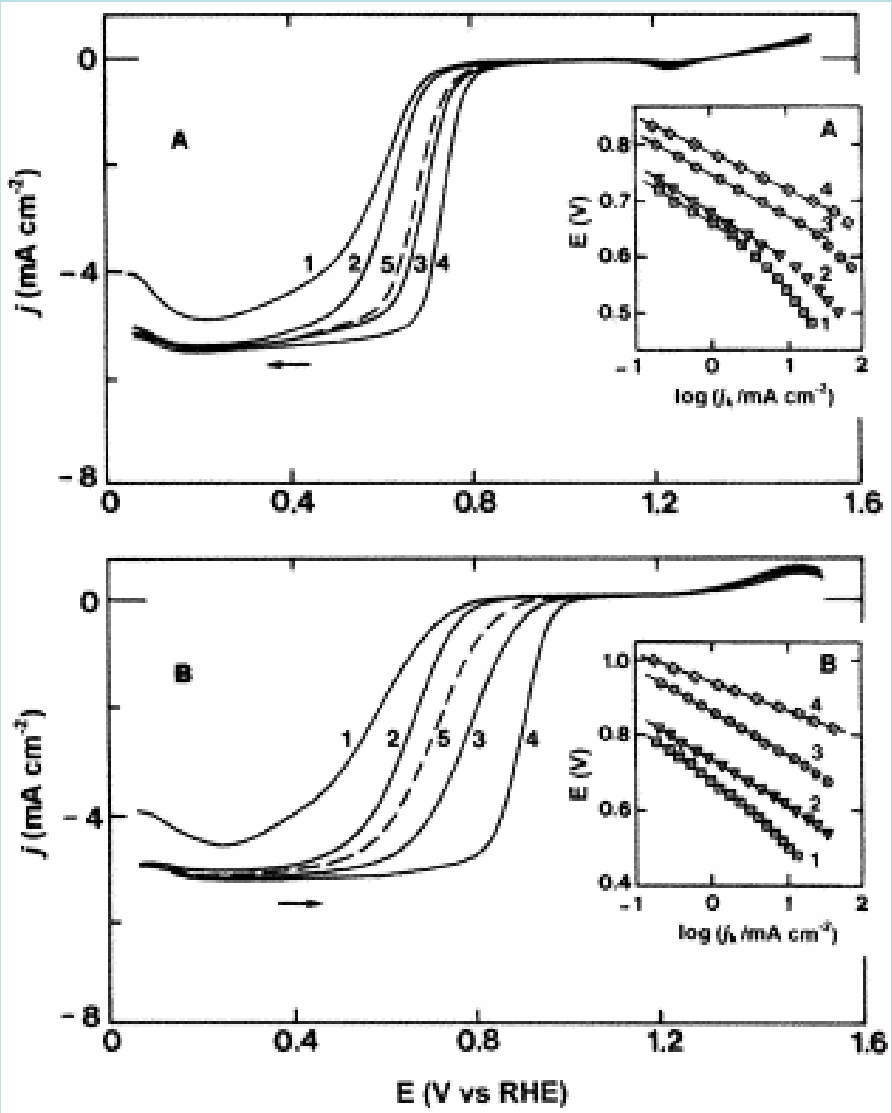


Fig. 11. Current–potential curves for oxygen reduction on Pt(Cu_{xs})/Au rotating-disc electrodes in O_2-saturated 0.1 M $HClO_4$ (dE/dt = 20 mV s^{-1}). Rotation rate f = 1100 rpm.

$t_{Cu,\,dep}$: (1) 3 s; (2) 10 s; (3) 40 s; (4) 60 s; (5) 120 s

$t_{Pt,\,repl}$ = 180 s

The insets show mass-transport corrected Tafel plots.

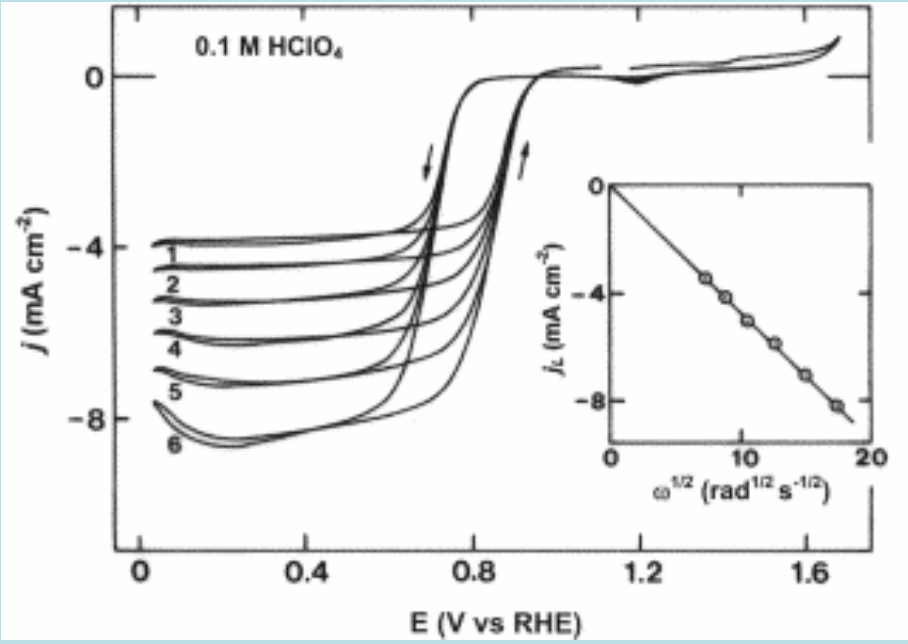


Fig. 12. Current–potential curves for oxygen reduction on Pt(Cu)/Au rotating-disc electrodes in O_2-saturated 0.1 M $HClO_4$ (dE/dt = 20 mV s^{-1}). Rotation frequency:

f = (1) 8.33; (2) 12.5; (3) 18.33; (4) 25; (5) 33.33; (6) 50 Hz.

$t_{Cu,\ dep}$ = 60 s

$t_{Pt,\ repl}$ = 180 s

The inset shows plot of j_L vs. $\omega^{1/2}$.

- The catalytic activity of the Pt(Cu)/Au electrode for oxygen reduction depends on the amount of copper deposited and exchanged by Pt.
  The half-wave potential increases as the amount of copper is increased, until it reaches a maximum value for 60 s of copper deposition.

- A remarkable hysteresis was observed between the forward (negative) and the backward (positive) potential scan. Reduced platinum clusters exhibit higher catalytic activity than oxidized platinum clusters.

- The catalytic activity of reduced Pt(Cu)/Au surface is significantly higher than the activity of reduced smooth polycrystalline Pt surface.

Pt-M AND Au-M BIMETALLIC ELECTROCATALYSTS (M = Pb, Cu, Fe, Co, Ni) PREPARED BY A GALVANIC REPLACEMENT PROCESS

G.Kokkinidis, S.Sotiropoulos

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

favourable exchange

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

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.

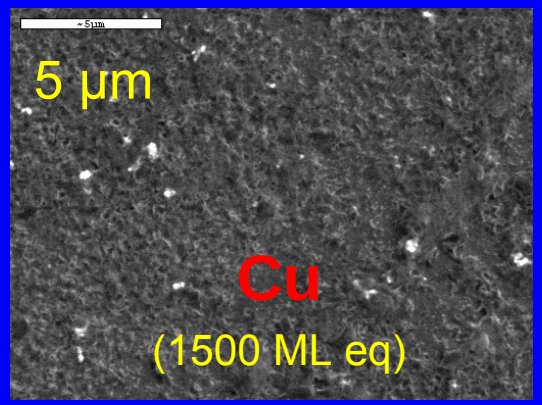
➢ Electrochemical treatment (positive potentials):

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

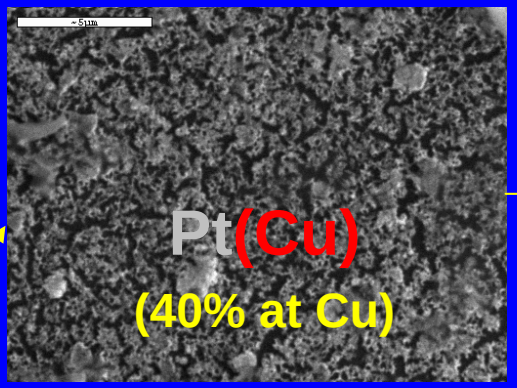
➢ Room temperature during all process steps (no annealing):

- skip energy and labour intensive step
- alloy formation at low temperature?

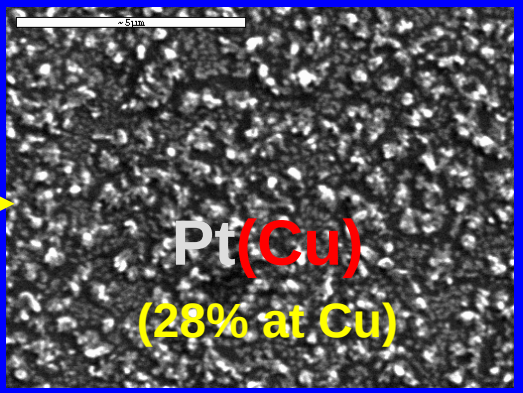
SEM and EDS of indicative M, Pt(M) and Au(M) deposits

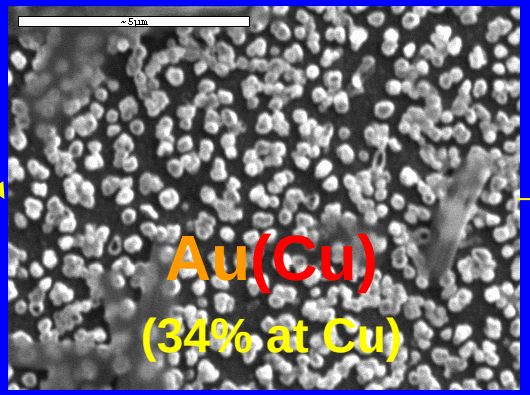


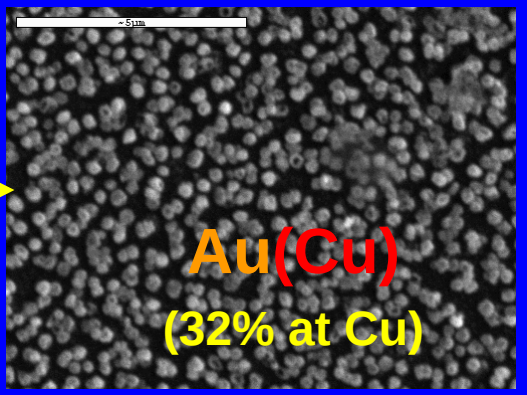
exchange



activation

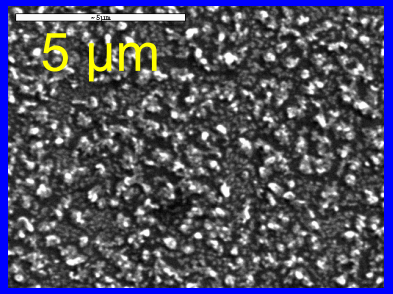




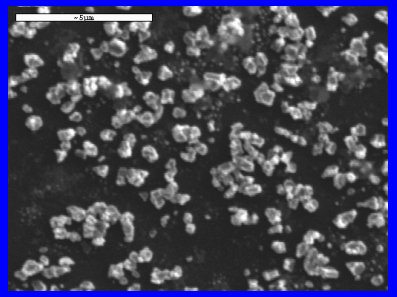


SEMs of M, Pt(M) and Au(M) tested

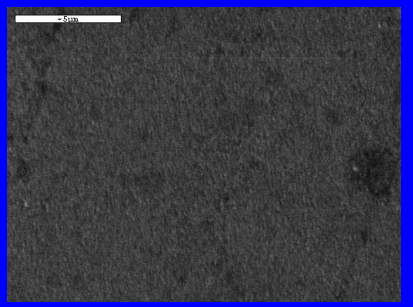
Pt(Cu 28%)
(from1500 ML)



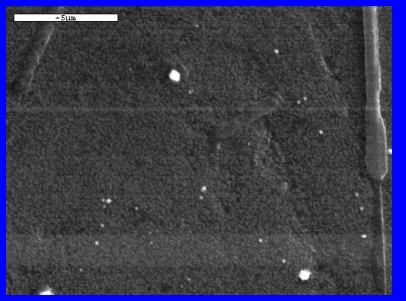
Pt(Pb 27%)
(from1000 ML)

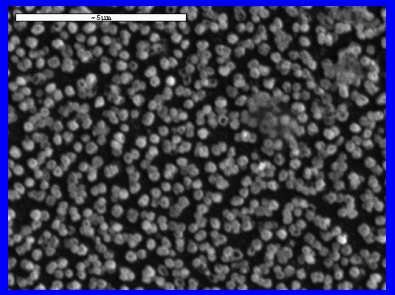


Pt(Ni 23%)
(from 300 ML)

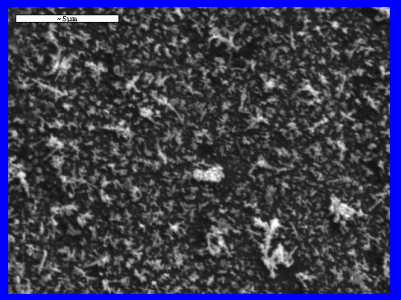


Pt(Co 27%)
(from 300 ML)

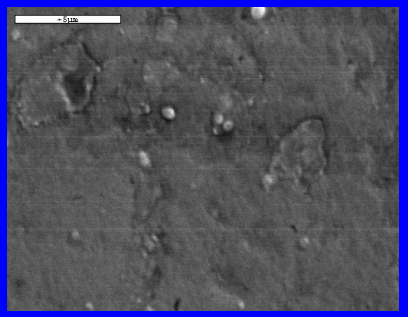




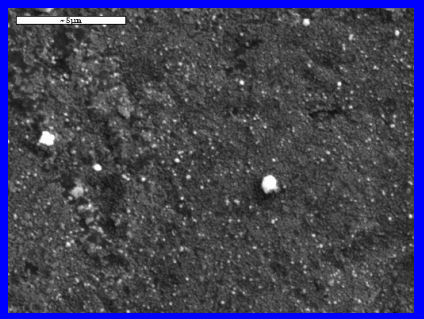
Au(Cu 32%)
(from1500 ML)



Au(Pb 20%)
(from1000 ML)

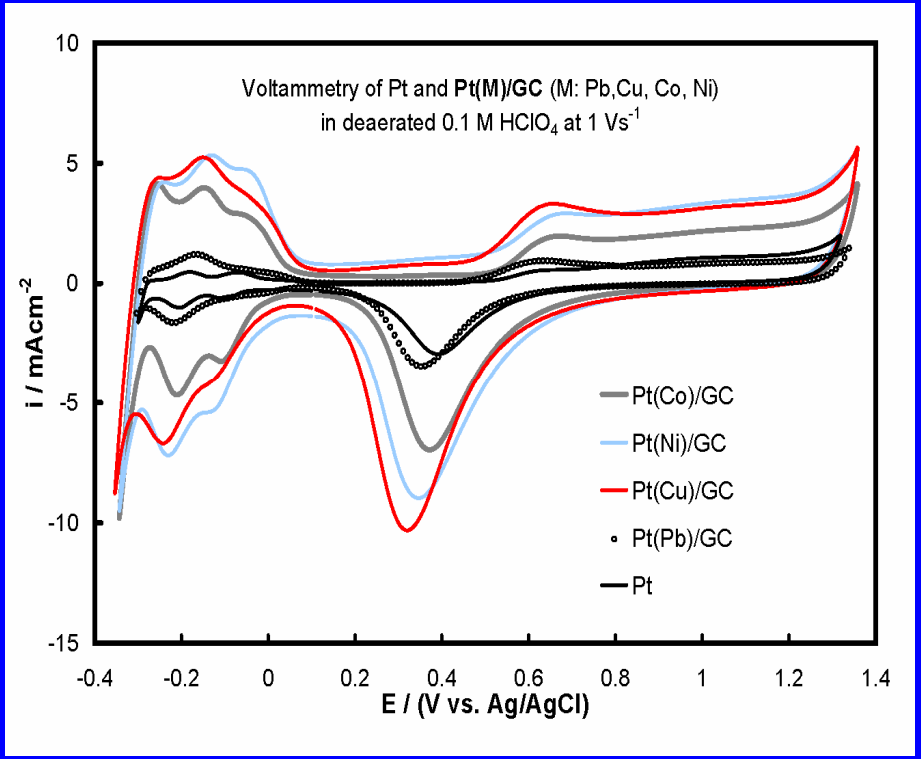


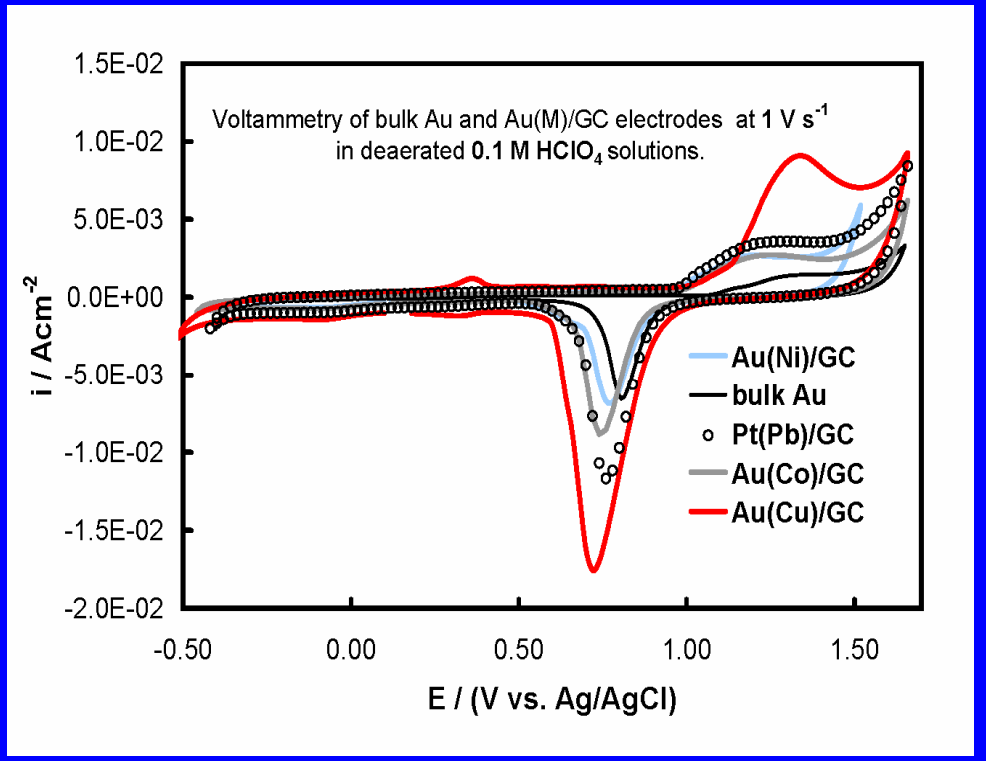
Au (Ni 5%)
(from 300 ML)



Au (Co 4%)
(from 300 ML)

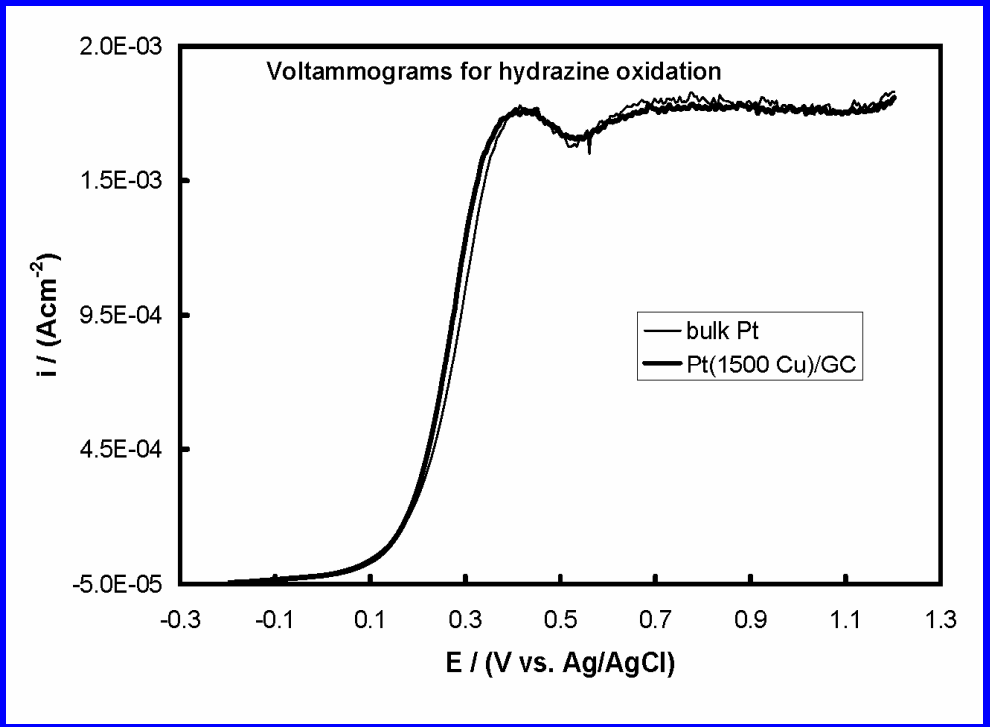
Electrochemical characterisation-I



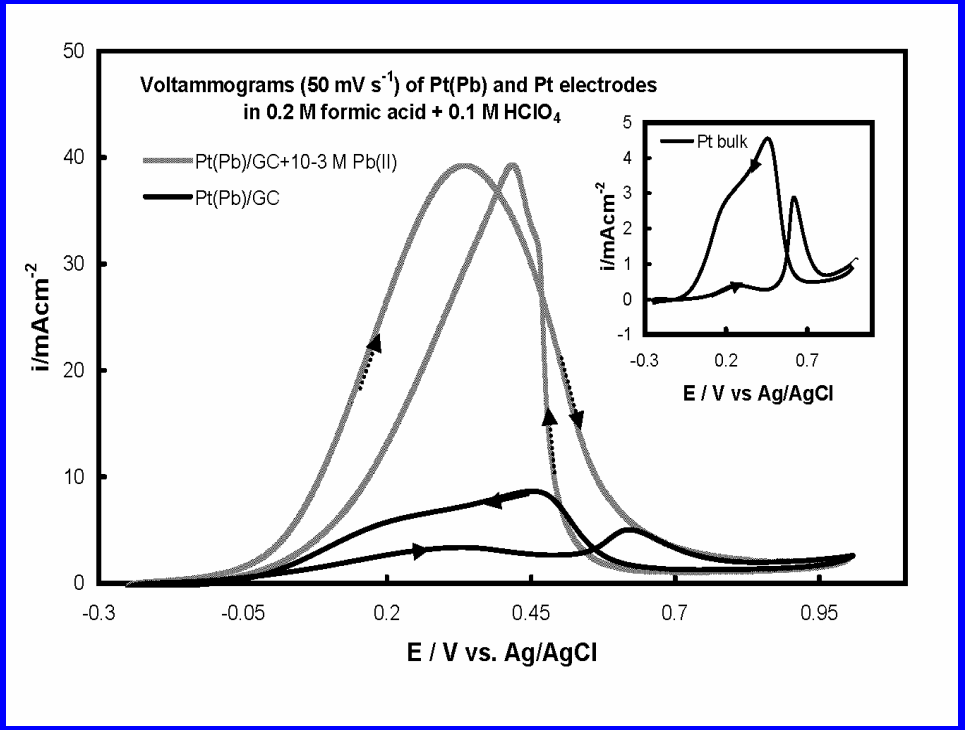


- Surface electrochemistry same as of bulk Pt and Au: only Pt or Au on the surface
- Electroactive surface areas: 2-8 - fold increase from geometric area

Electrochemical characterisation-II



Hydrazine oxidation on Pt(Cu)

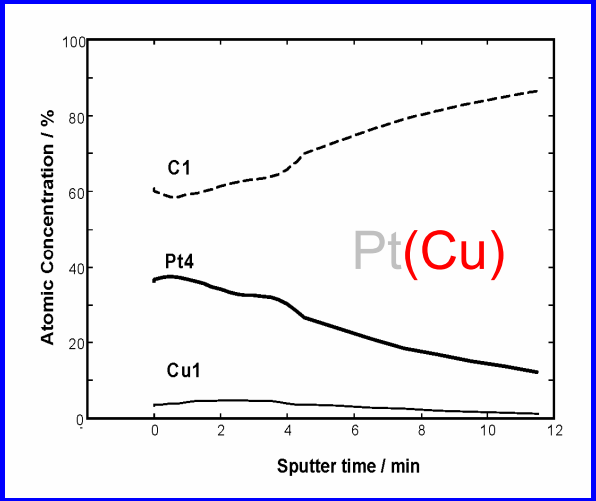


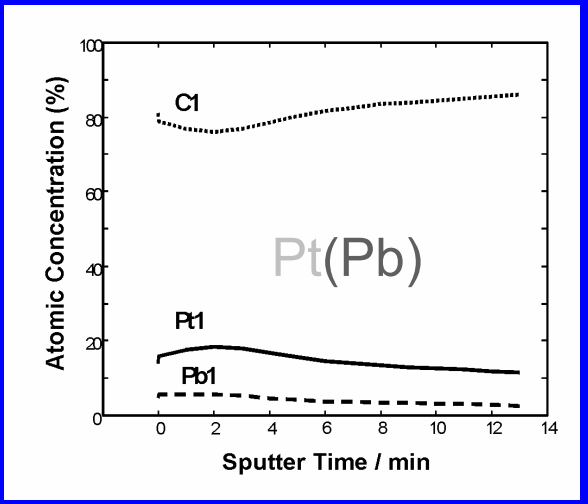
Formic acid oxidation on Pt(Pb)

- 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

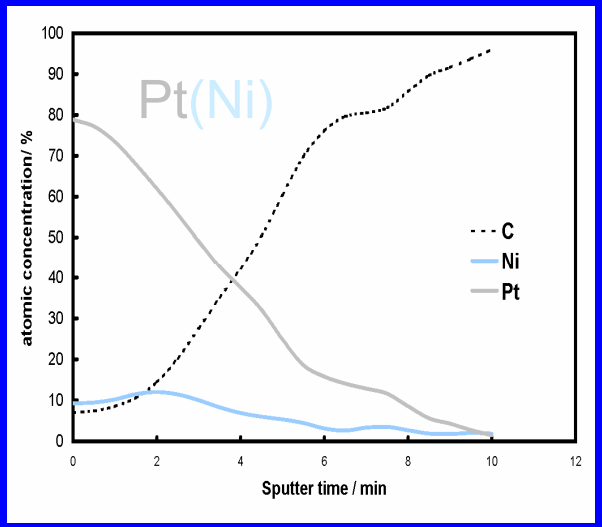
Pt and Au shell - bimetallic core (Pt-M, Au-M) electrocatalysts

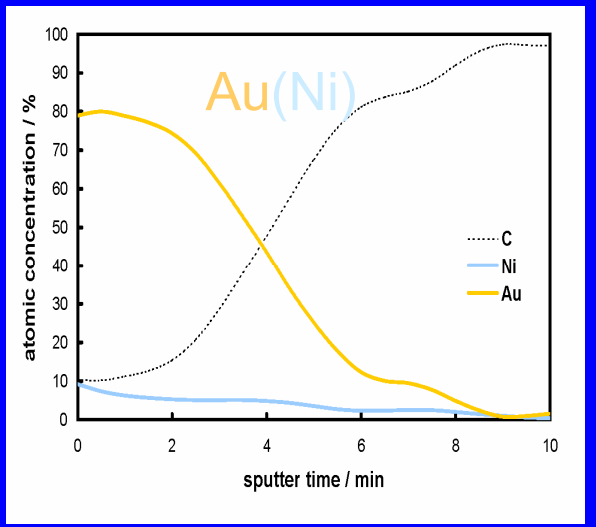
Sputter-etch AES characterisation





- 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

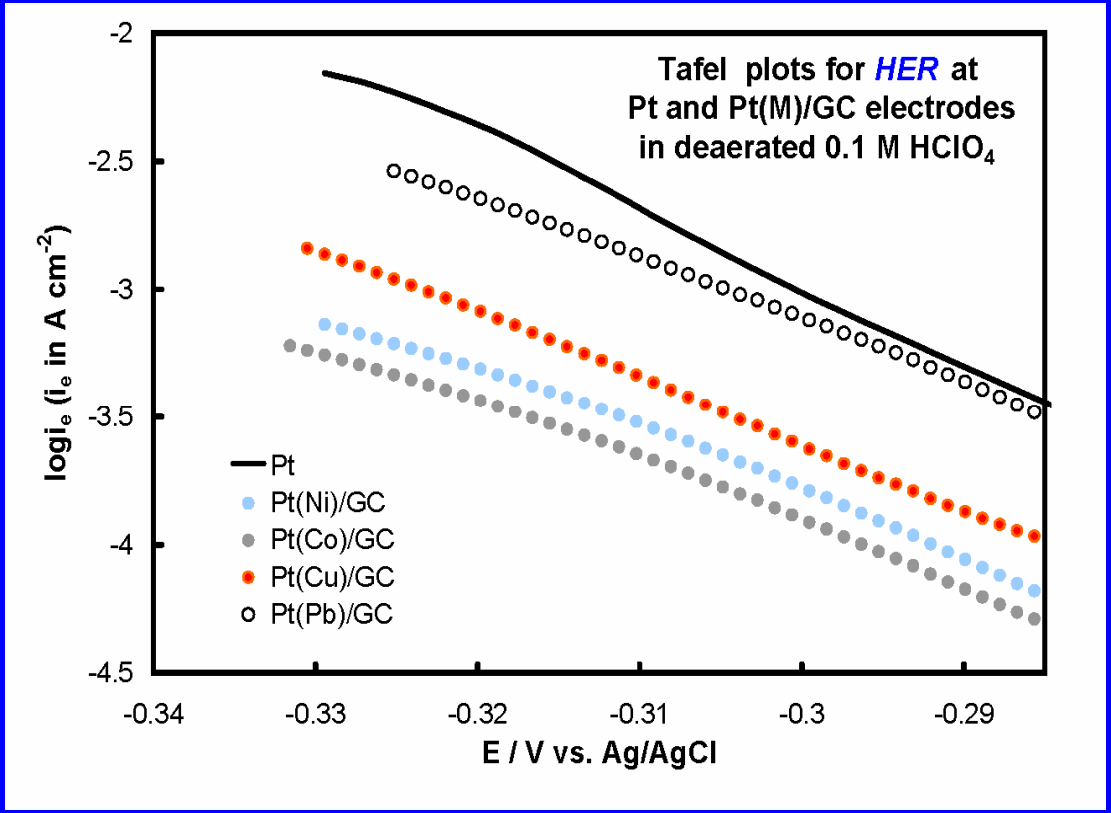




XRD characterisation

- alloy formation (at room temperature)
- Pt crystallite size: 7-11 nm
  Au crystallite size: 10-15 nm

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 (ε_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**

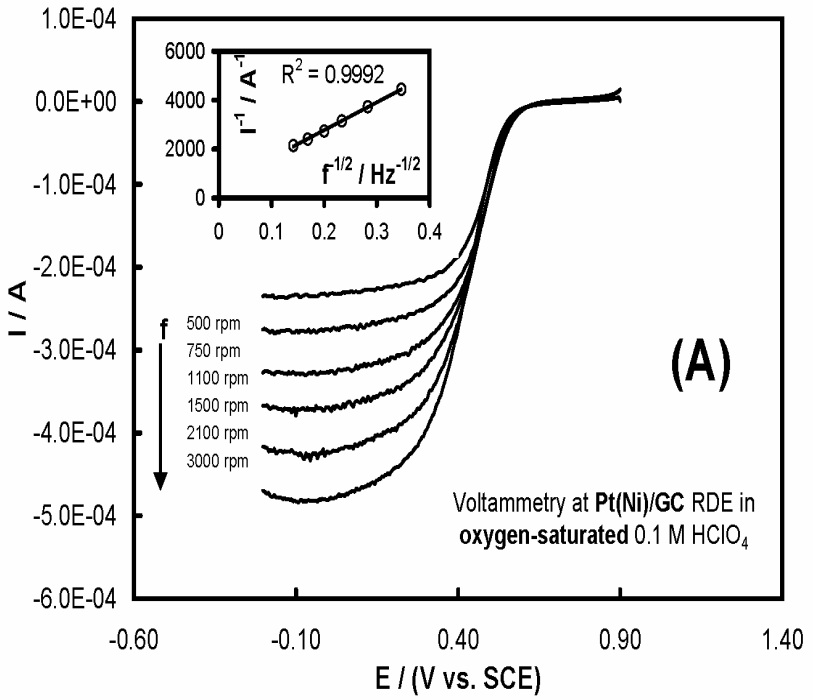
(intermediate M-H bond strength)

- unaffected HER at Pt(Pb):

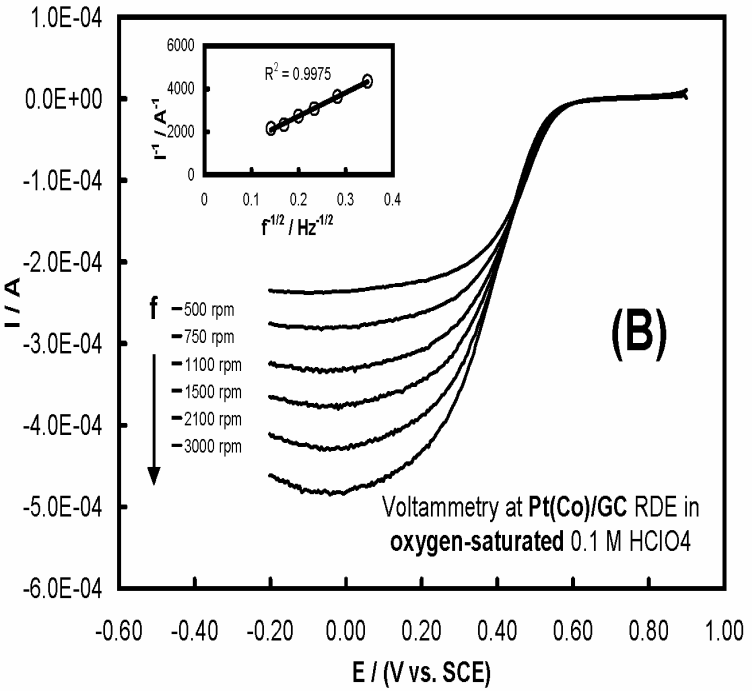
no DFT predictions; lower Wegner-Scheizer radius but higher Pauling electronegativity

Oxygen reduction reaction (*ORR*)

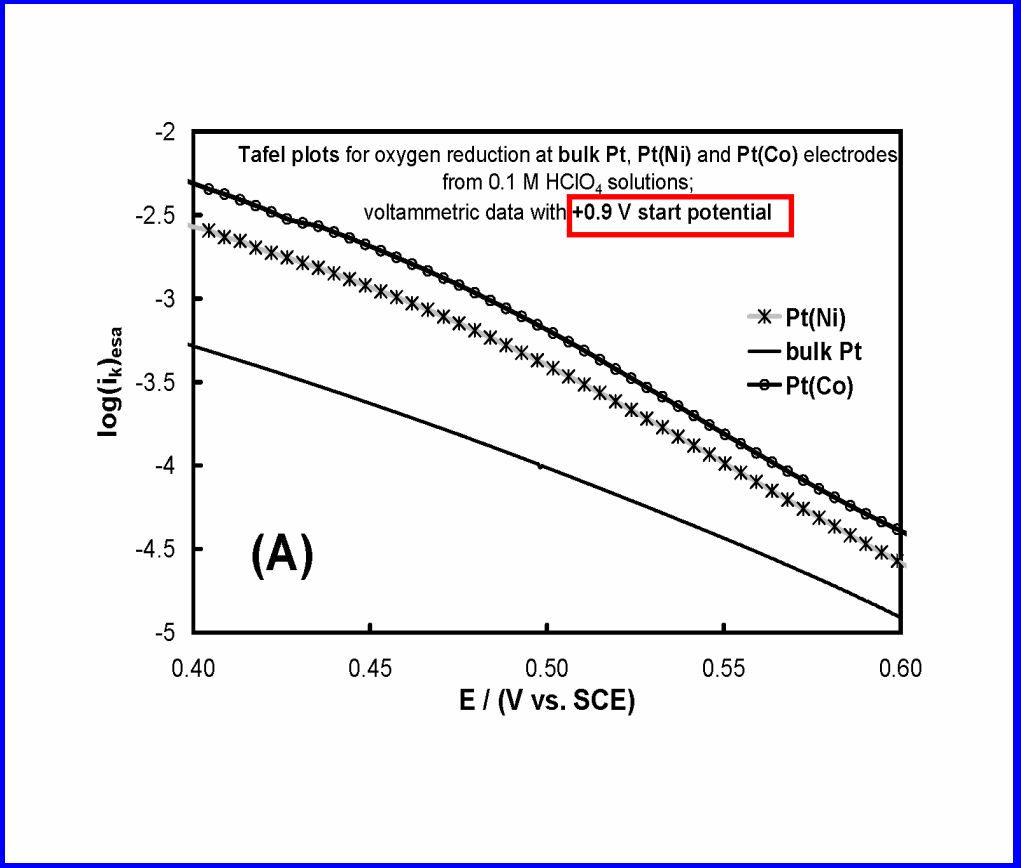
Pt(Ni) /GC



Pt(Co) /GC



Oxygen reduction reaction (*ORR*)



* Depending on start potential and the amount of oxides initially present; when +1.2 is used, a slight decrease is observed.

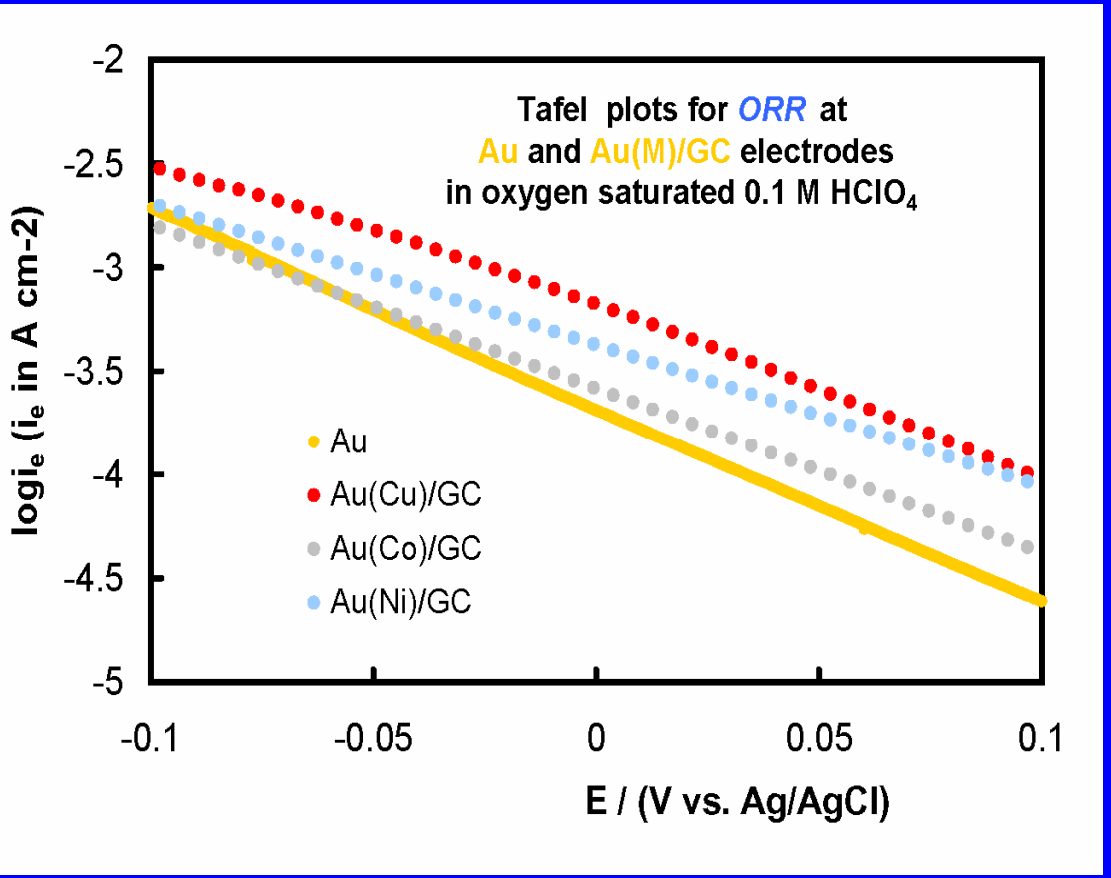
- **promotion* of ORR** at Pt(Co), Pt(Ni):

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

Pt ε_d down-shift due to larger ligand and strain effects by **non-alloyed M** regions in the core

- Markovic, Adzic, Mavrikakis: decrease of Pt-O strength.
- Watanabe, Sotiropoulos: increase of O-O scission.

Oxygen reduction reaction (*ORR*)

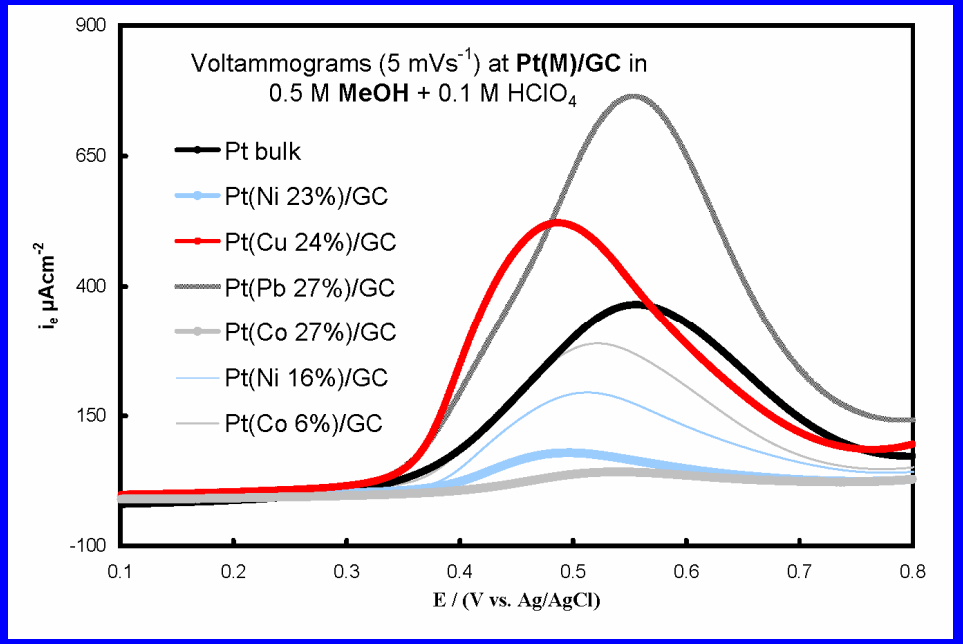


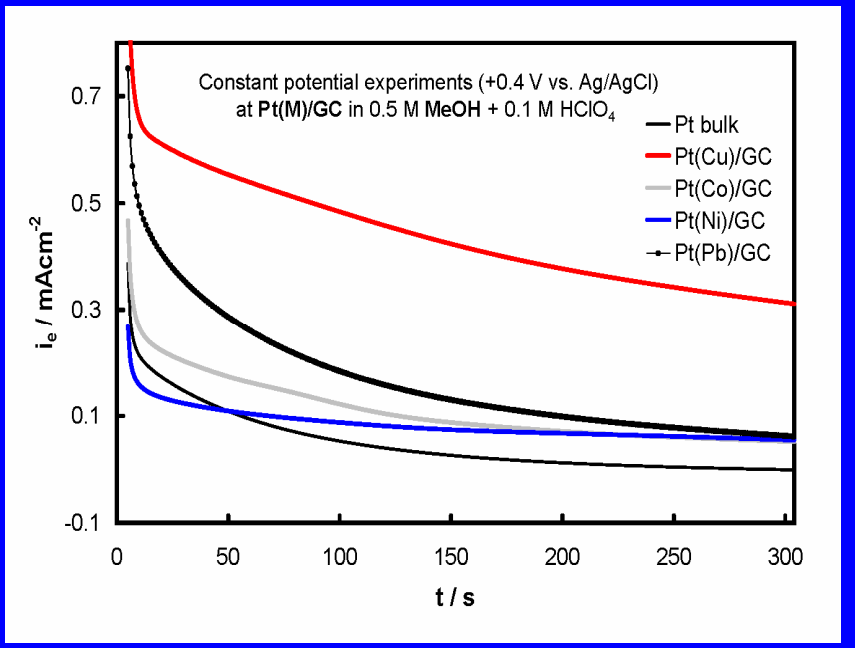
- enhancement of ORR at Au(Cu), Au(Ni) and Au(Co):

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

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

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 ε_d downshift and adsorption affinity →best performance

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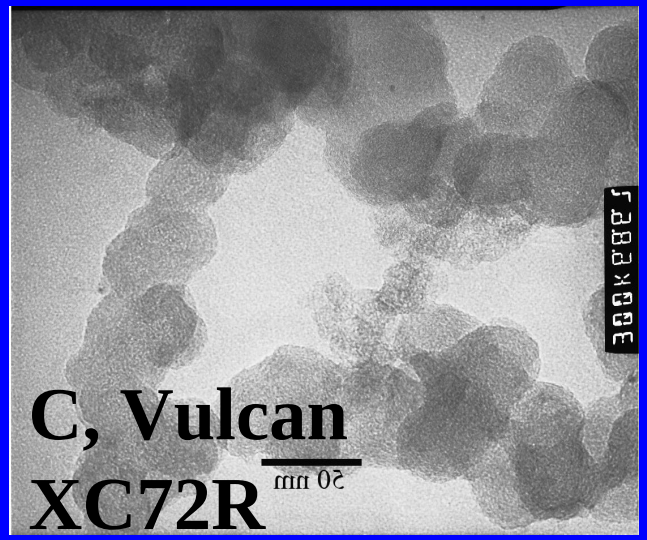
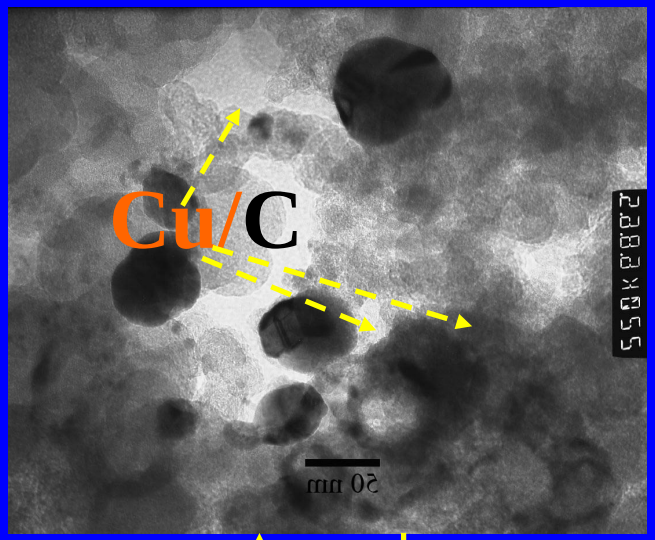
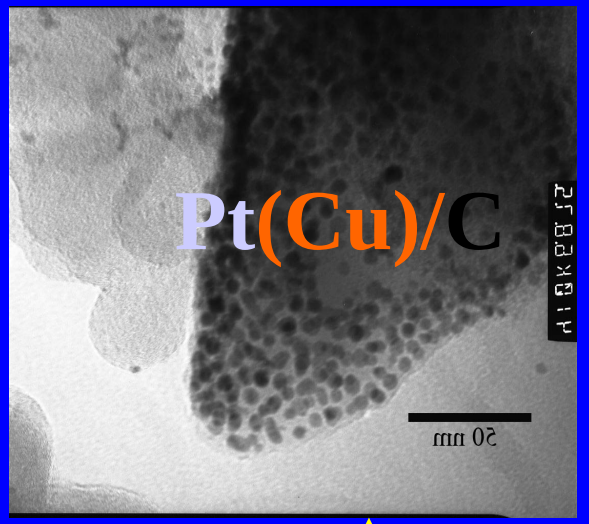
Towards the application of the method to practical catalysts







Impregnation-

Wet reduction ($NaBH_4$)

Transmetalation (K_2PtCl_6)

TEM micrographs of Vulcan XC72R carbon, Cu/C precursor catalyst, and Pt(Cu)/C catalyst.

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

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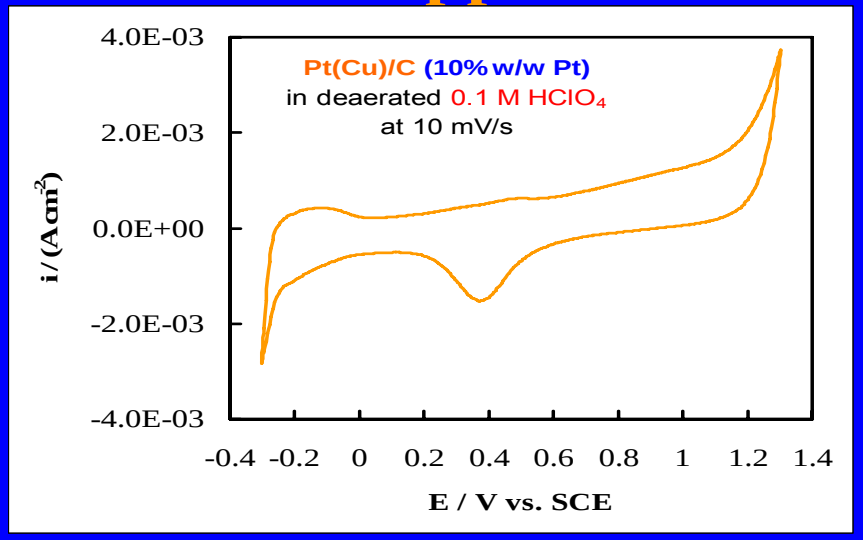

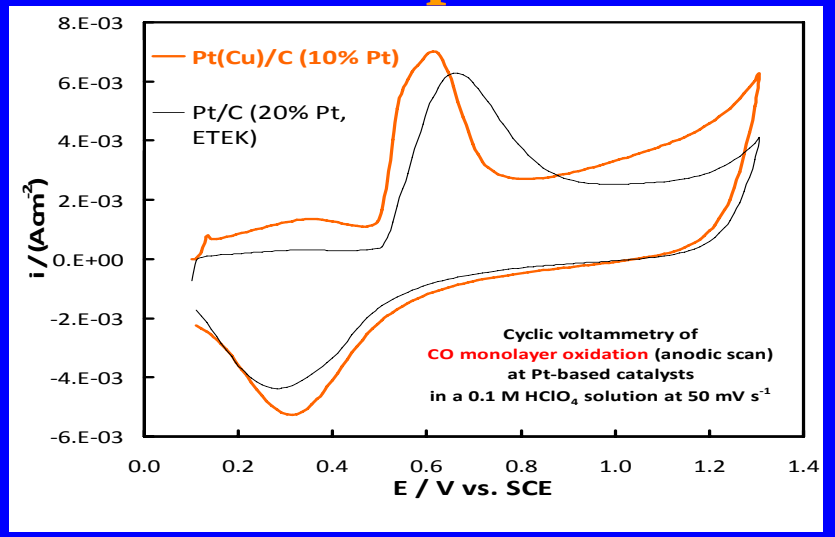

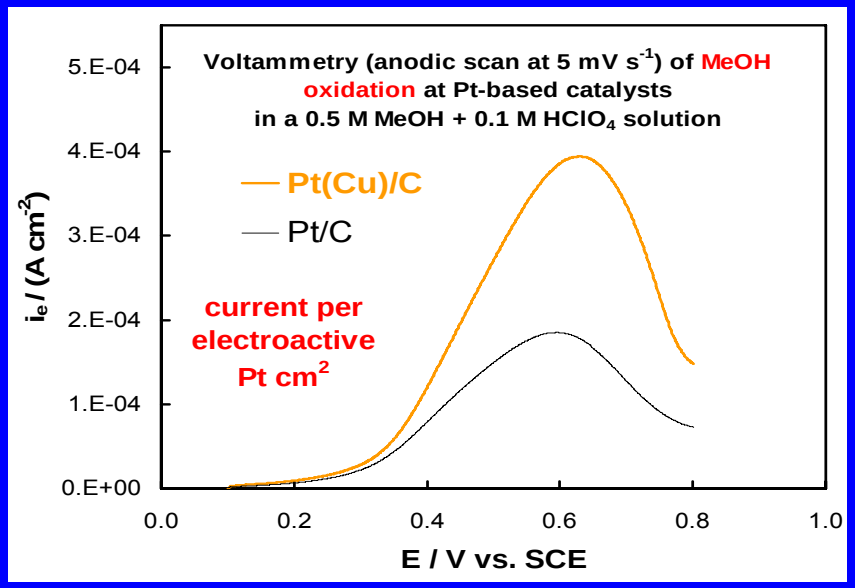

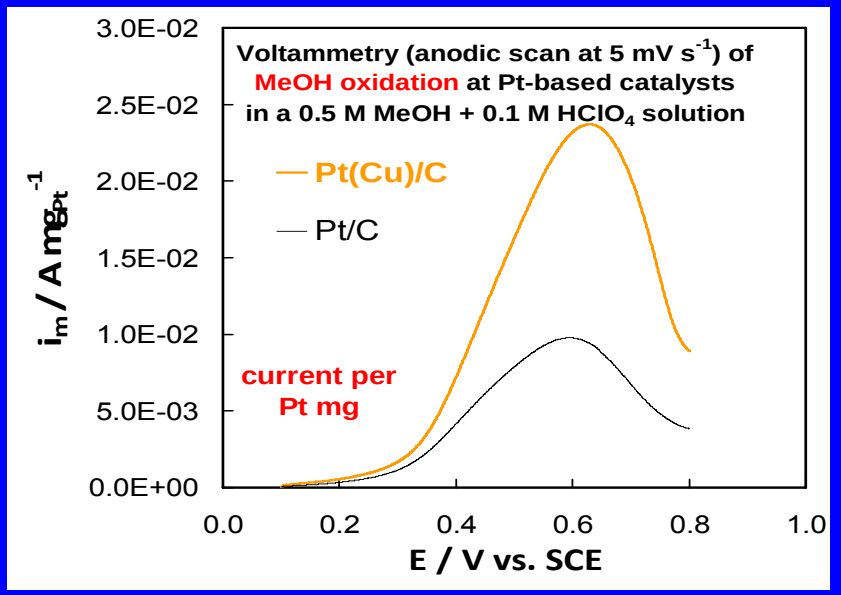

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Aristotle University

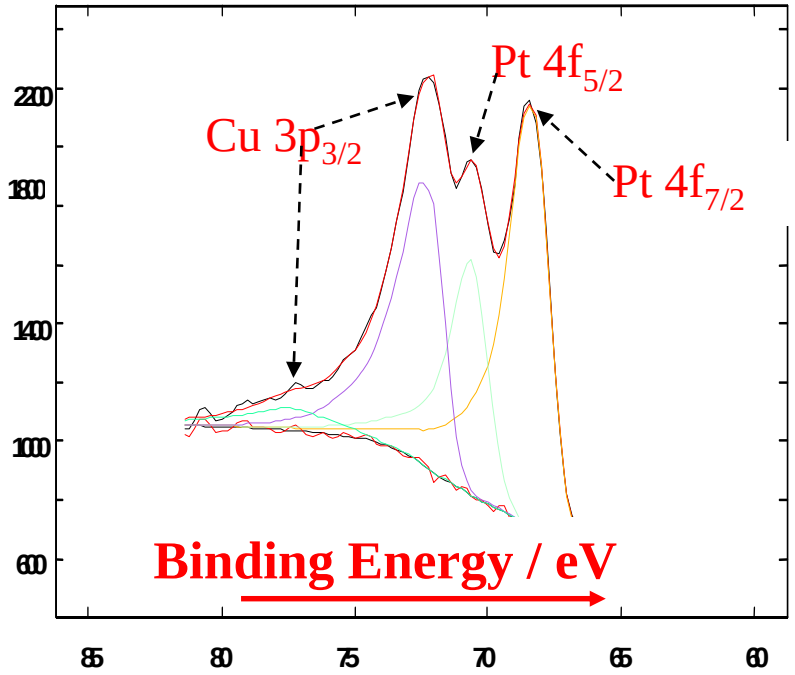
Summary / Potentialities

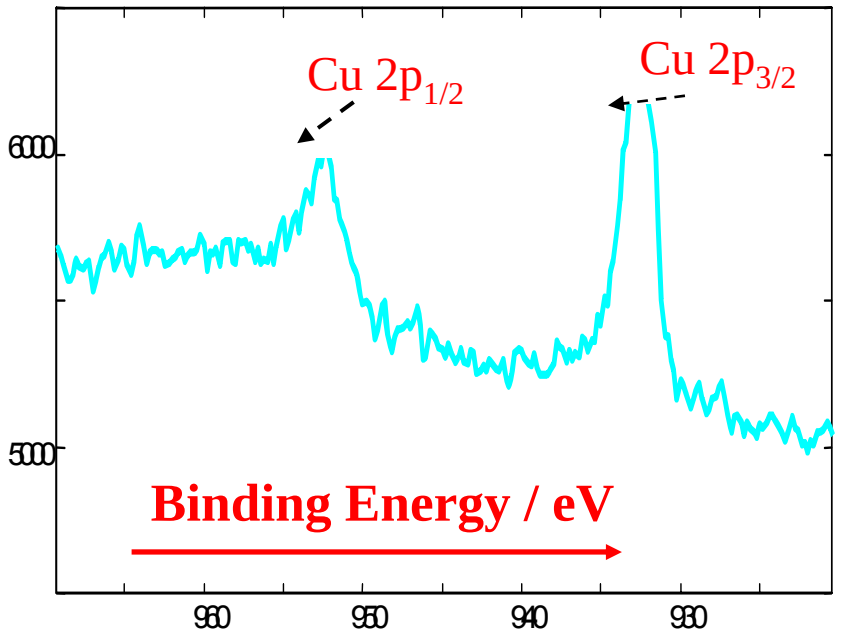
- Transmetalation can be used for the production of catalysts with a **Pt (or Au) shell** and a **bimetallic Pt-M (or Au-M) core** (M: Pb, Cu, Co, Ni,…)
  - Two step, low temperature modification of GC support electrodes
  - One-step, low temperature modification of carbon powders

- Pt(M) and Au(M) showed modified catalytic activity even without annealing
  - Pt(M) suppresed ***HER*** (potential for hydrogenation reactions)
  - Pt(M) enhanced ***ORR***
  - Pt(M) improved CO tolerance for ***MOR*** (especially Pt(Cu))
  - Pt(M) improved ***BOR*** ; **Pt-Au(M) mixed catalysts** possible

SUPPLEMENTS

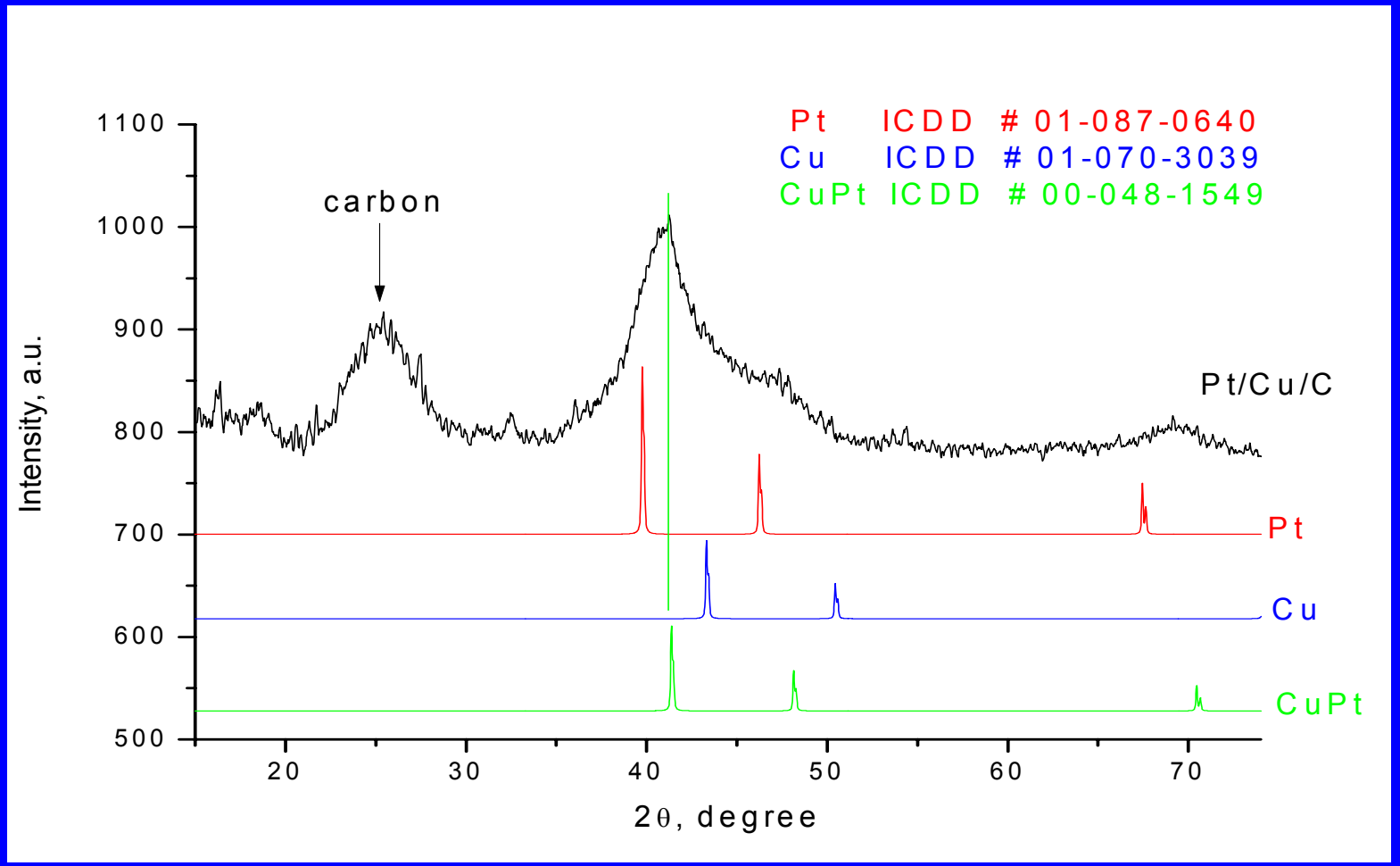
Pt and Au shell - bimetallic core (Pt-M, Au-M) electrocatalysts





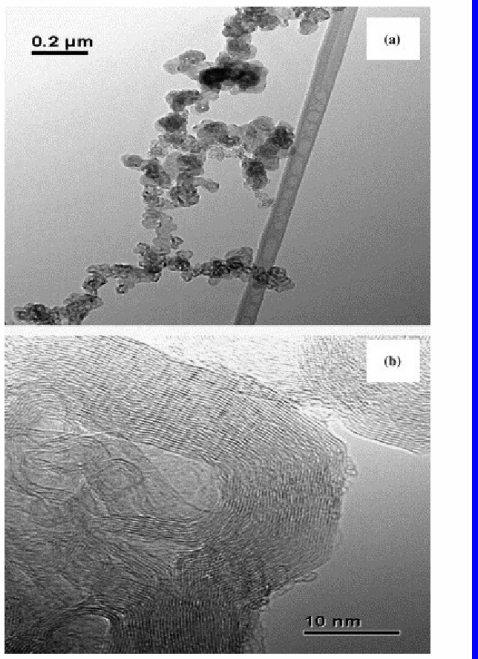
XPS spectra of the Pt(Cu)/C catalyst in the low and high energy ranges.

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



XRD spectrum of the Pt(Cu)/C catalyst.

Towards the application of the method to practical catalysts



Pure Black Carbon (PB)

(Barsukov and co-workers)

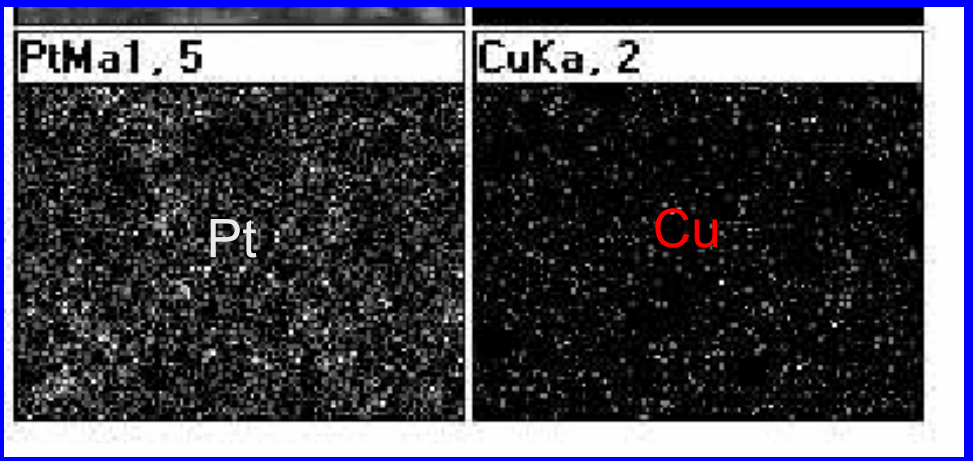
Impregnation

H_2 annealing

30% Cu/PB → Pt(Cu 50%)/PB

+Nafion

Pt(Cu 50%)/PB/GC



Towards the application of the method to practical catalysts