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Multistage Electrodeposition of Supported Platinum-based Nanostructured Systems for Electrocatalytic Applications

T. S. Mkwizu, M.R. Modibedi and Mkhulu K. Mathe*

***kmathe@csir.co.za**

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Overview

- Acknowledgements
- Rationale
- Chemical routes to Nanoparticulate Multimetallic Electrocatalysts
- Experimental Approach
- Results
- Conclusions

Acknowledgements

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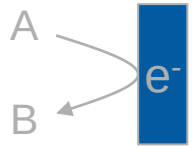
Introduction

- **Electrocatalysis** concerns rates of interfacial chemical reactions - between electrodes (solid surfaces) and molecules in solution or gas phase.

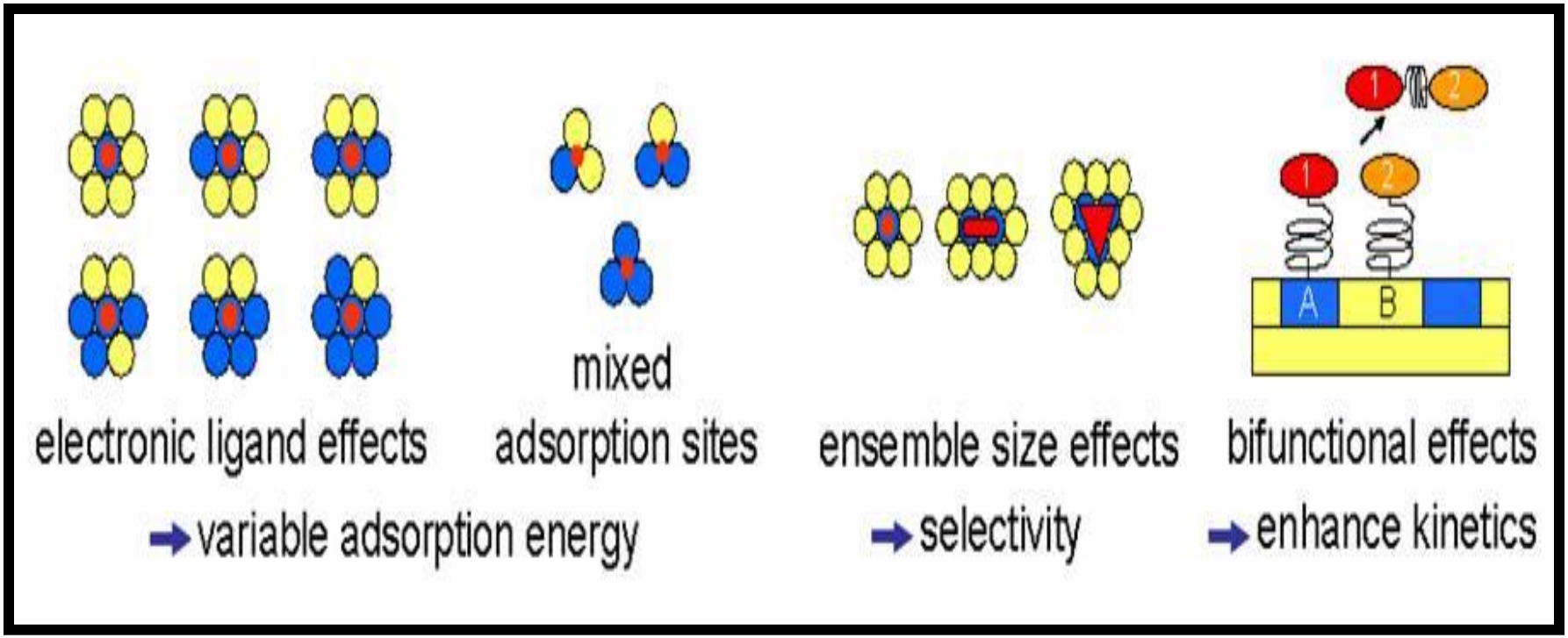


- Properties of electrodes (e.g. Catalytic/Electrocatalytic Activity) depend on variation of the **particle sizes**, **shapes**, and **dispersion** of constituent elements of the given electrode surface.

- Applications areas: Fuel cells, electrochemical sensors, electrolyzers

Introduction

Atomic-level processes during electrocatalysis

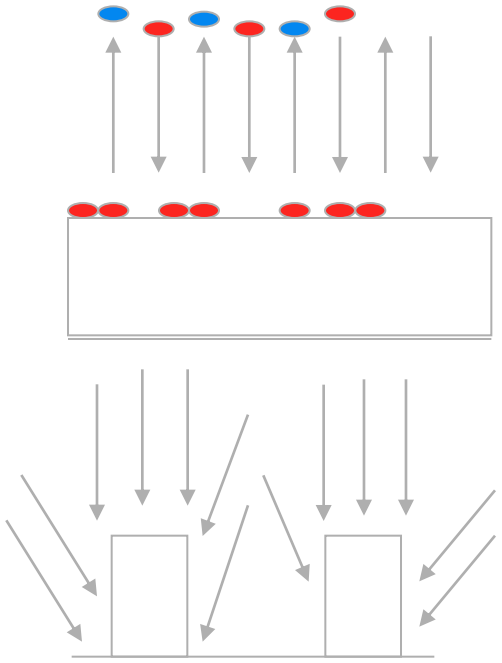


www.uni-ulm.de/.../Model_Electrocatalysis.htm

Catalytic Active Sites (Active reaction area)

Surface-to-Volume ratio

Transport of reactants and products

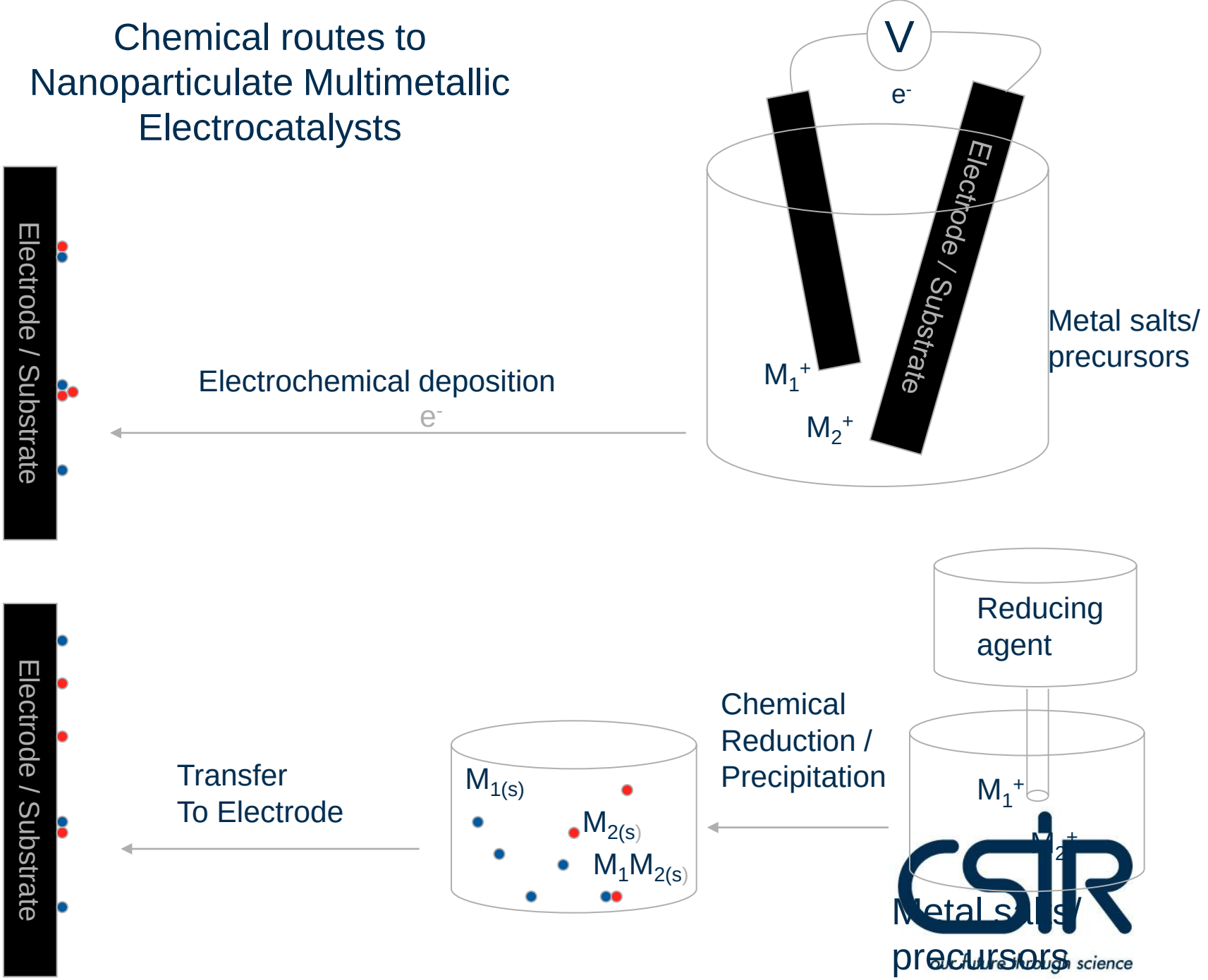


Thin Film

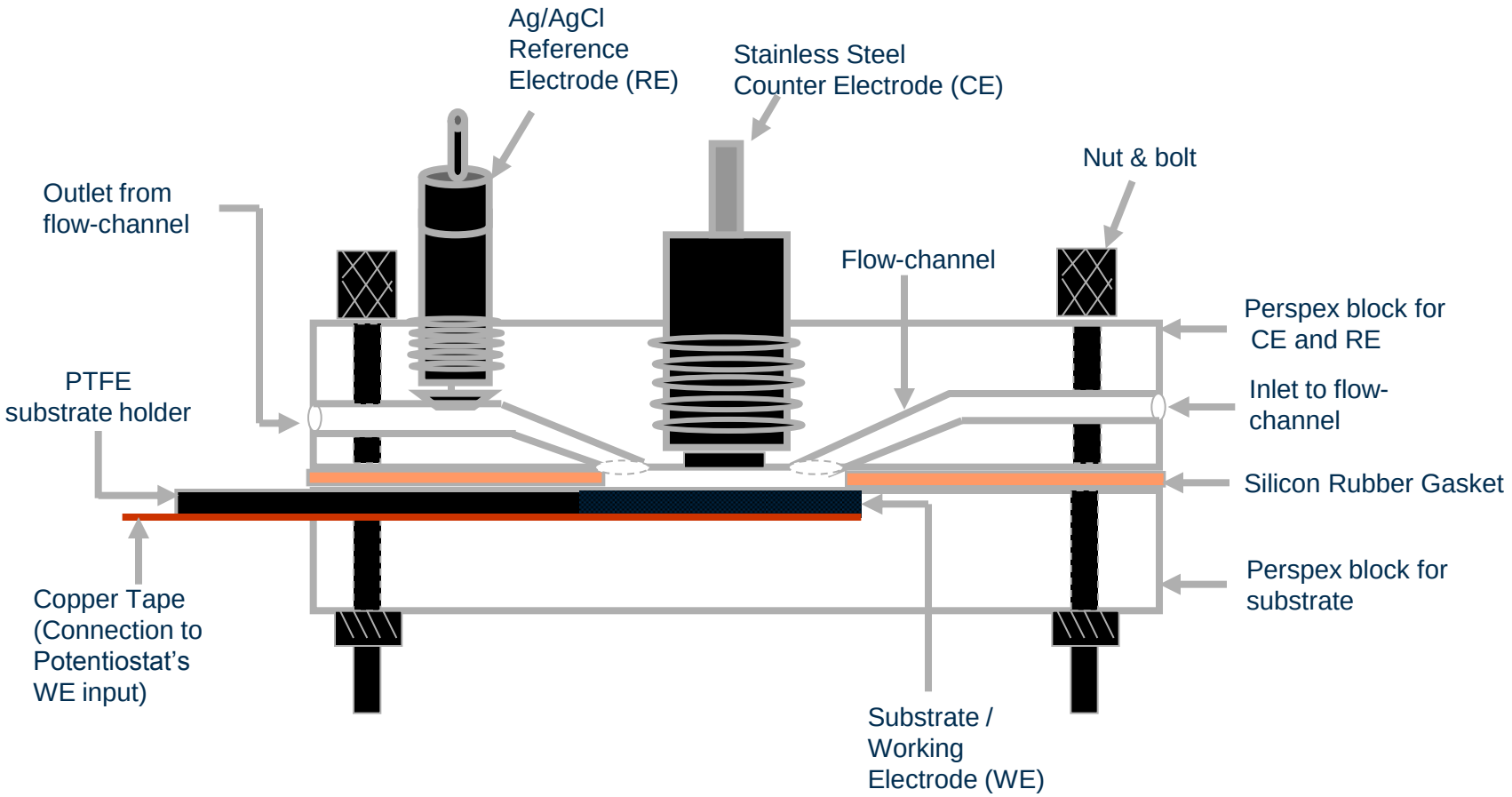
Nanostructures

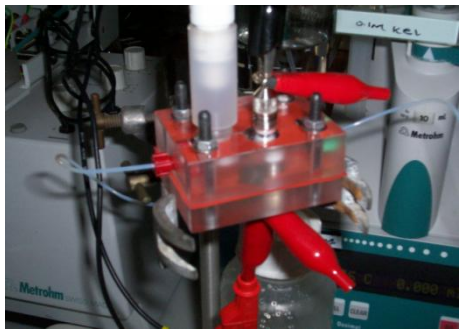
Electrocatalyst particles have to maintain electronic contact with support

Chemical routes to Nanoparticulate Multimetallic Electrocatalysts



Flow-cell setup





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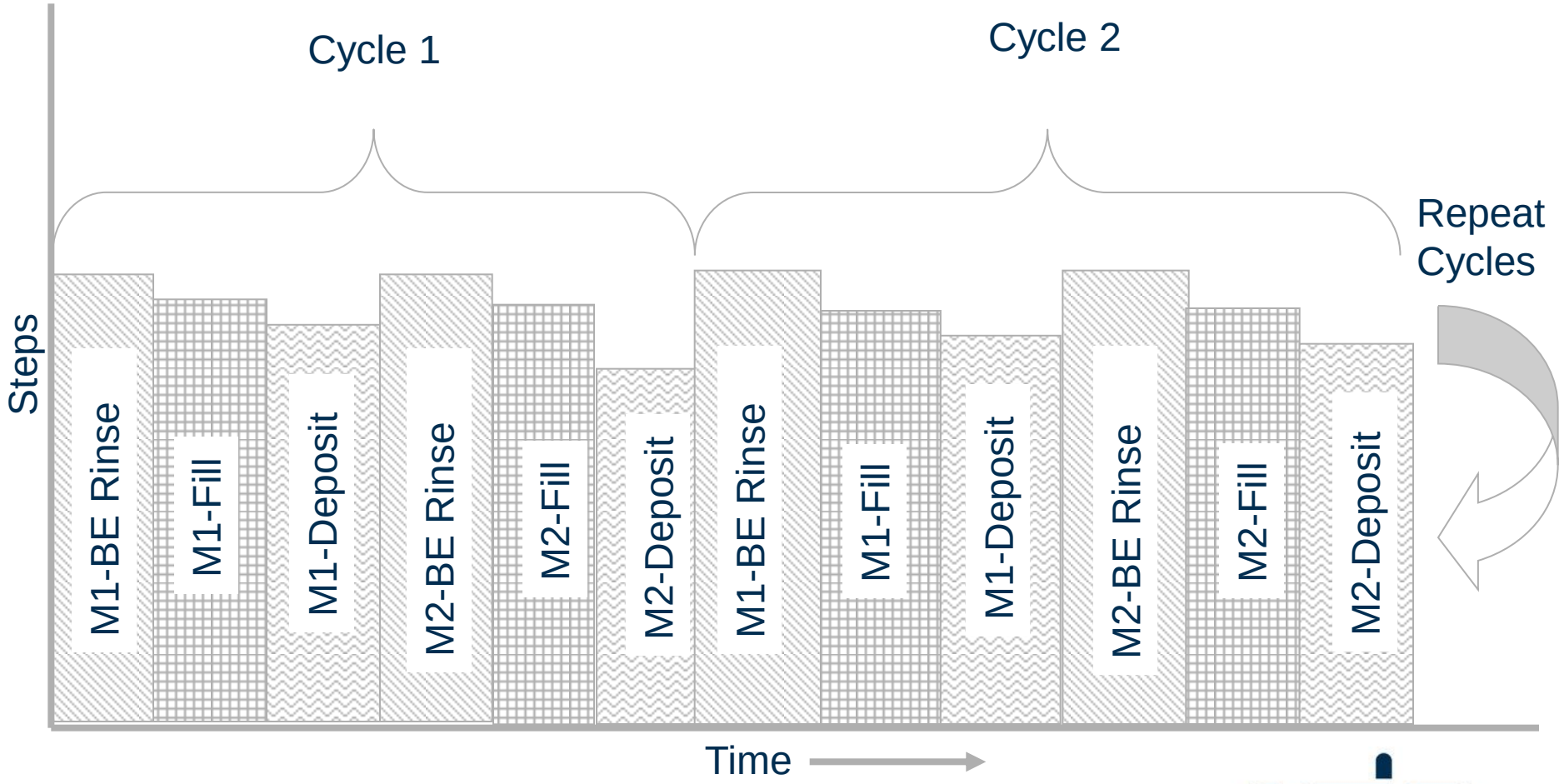
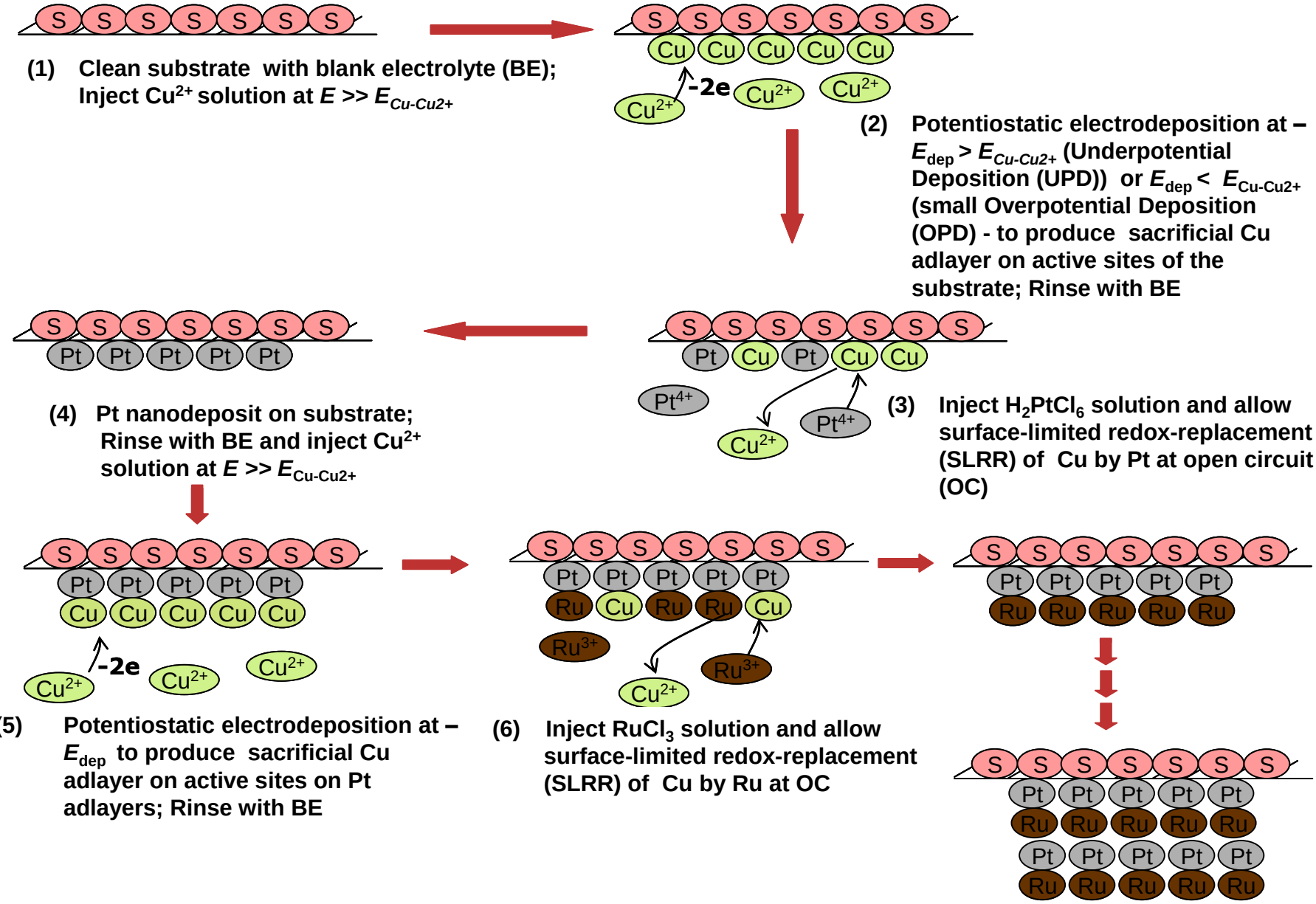
Sequential deposition



Noble-Metals studied = Pt, Ru, Au, Pd
Substrates = Carbon materials, Gold films

Sequential deposition coupled to Surface-limited Redox-replacement reactions (SLRR): Synthesis of multilayered bimetallic RuPt electrocatalyst



(1) Clean substrate with blank electrolyte (BE); Inject Cu^{2+} solution at $E >> E_{Cu\text{-}Cu2+}$

(2) Potentiostatic electrodeposition at – $E_{dep} > E_{Cu\text{-}Cu2+}$ (Underpotential Deposition (UPD)) or $E_{dep} < E_{Cu\text{-}Cu2+}$ (small Overpotential Deposition (OPD) - to produce sacrificial Cu adlayer on active sites of the substrate; Rinse with BE

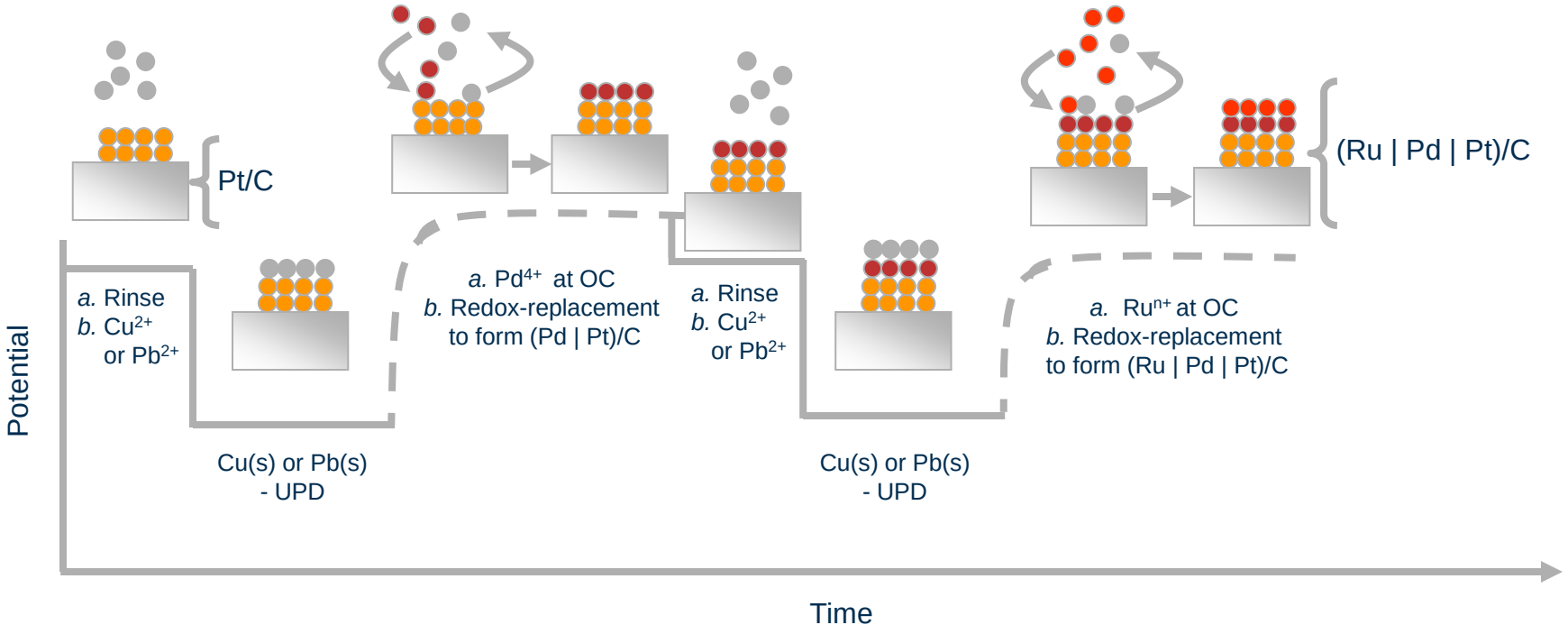
(3) Inject H_2PtCl_6 solution and allow surface-limited redox-replacement (SLRR) of Cu by Pt at open circuit (OC)

(4) Pt nanodeposit on substrate; Rinse with BE and inject Cu^{2+} solution at $E >> E_{Cu\text{-}Cu2+}$

(5) Potentiostatic electrodeposition at – E_{dep} to produce sacrificial Cu adlayer on active sites on Pt adlayers; Rinse with BE

(6) Inject $RuCl_3$ solution and allow surface-limited redox-replacement (SLRR) of Cu by Ru at OC

Multi-stage electrodeposition



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Substrates = Carbon materials, Gold films

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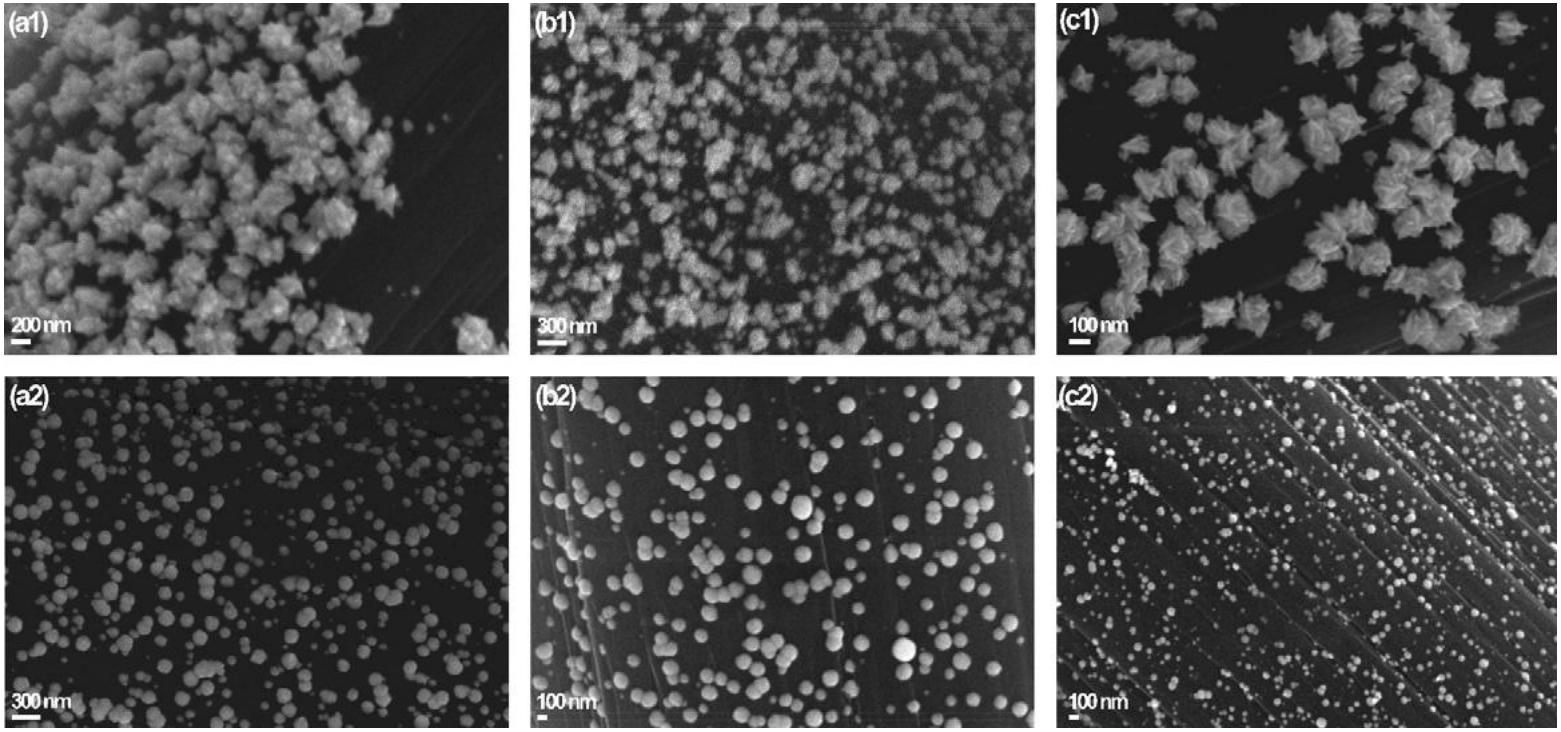
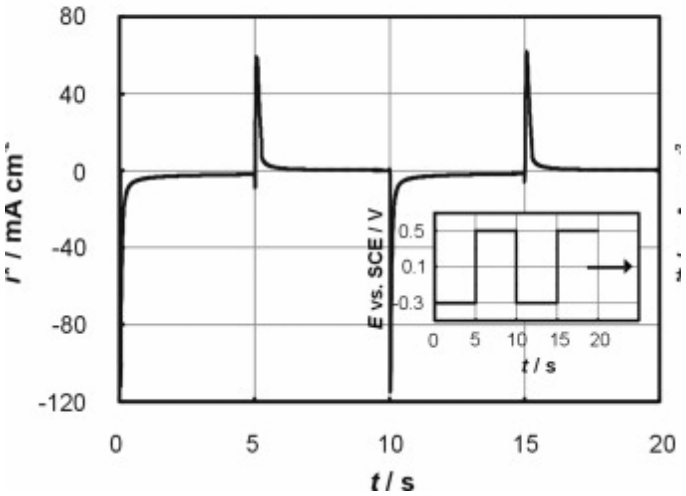
Example of Pulsed-Electrodeposition





Sieben et. al, Journal of Alloys and Compounds 509 (2011) 4002–4009

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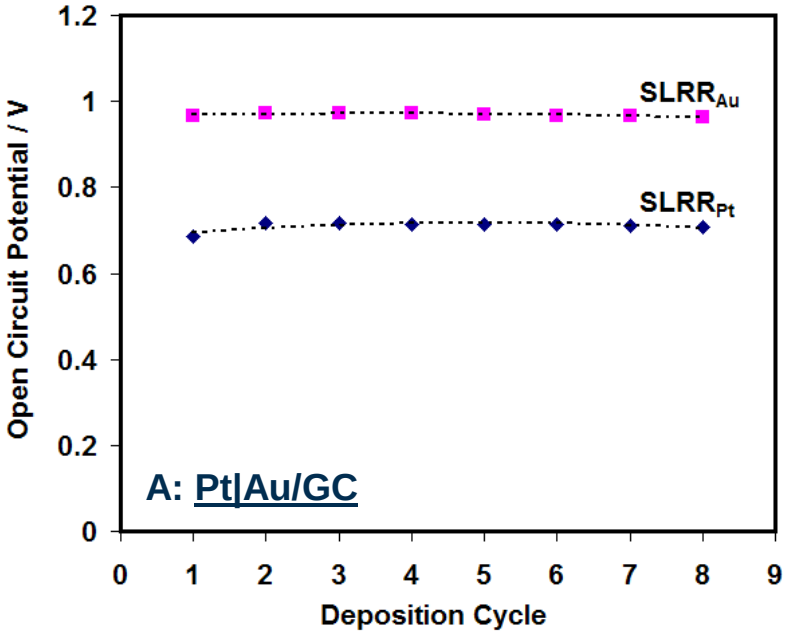
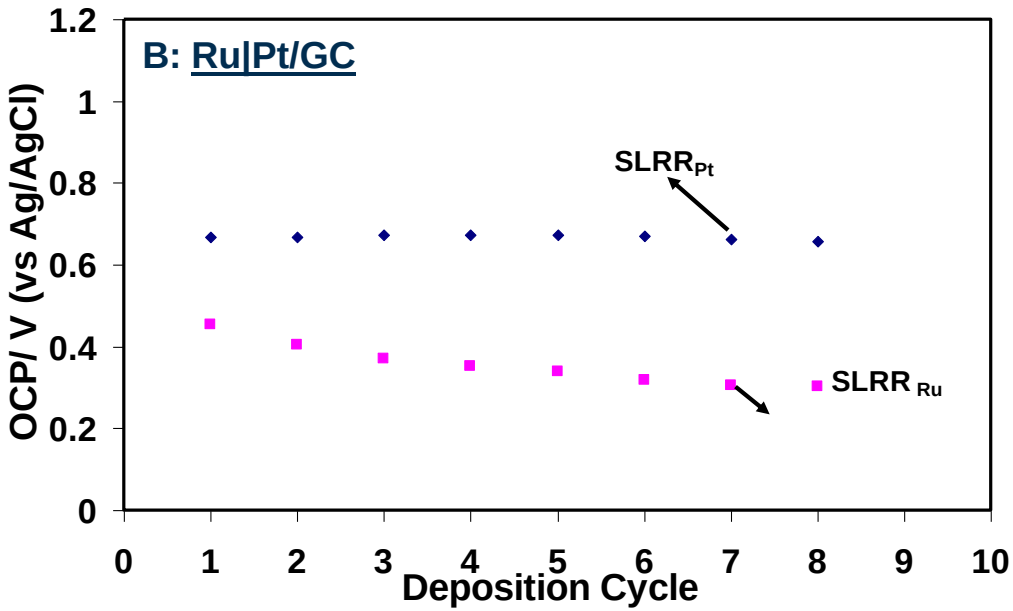
Maximum open circuit potential trends





OCP (w.r.t Ag/AgCl) during SLRR steps with during deposition of A and B

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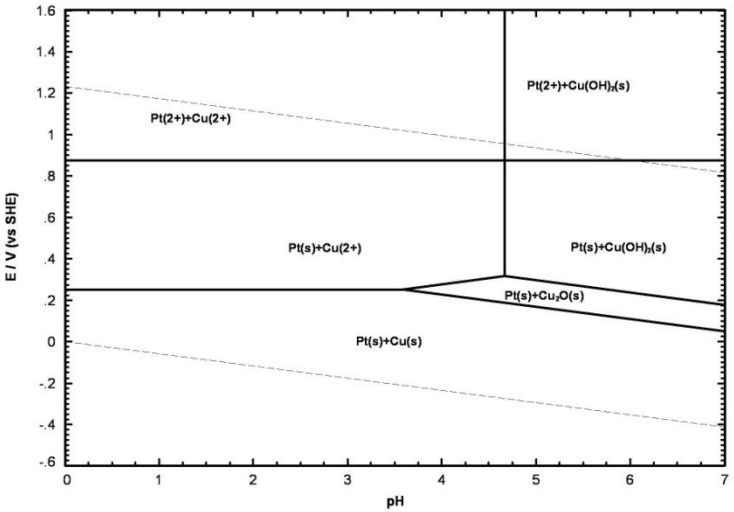
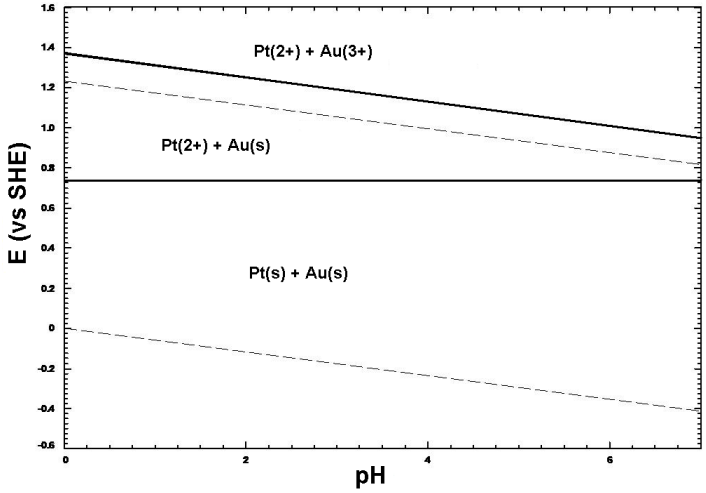
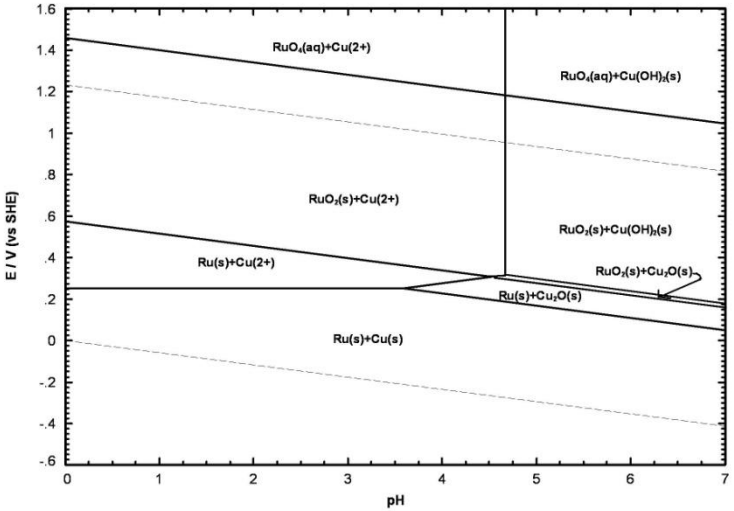
Thermochemical models



Pt-Cu-O-H at 298.15 K, 1 atm, fixed aqueous forms at 1 mol/Kg.



Pt-Au-O-H at 298.15 K, 1 atm, fixed aqueous forms at 1 mol / Kg.



Ru-Cu-O-H at 298.15 K, 1 atm, fixed aqueous forms at 1 mol/Kg.

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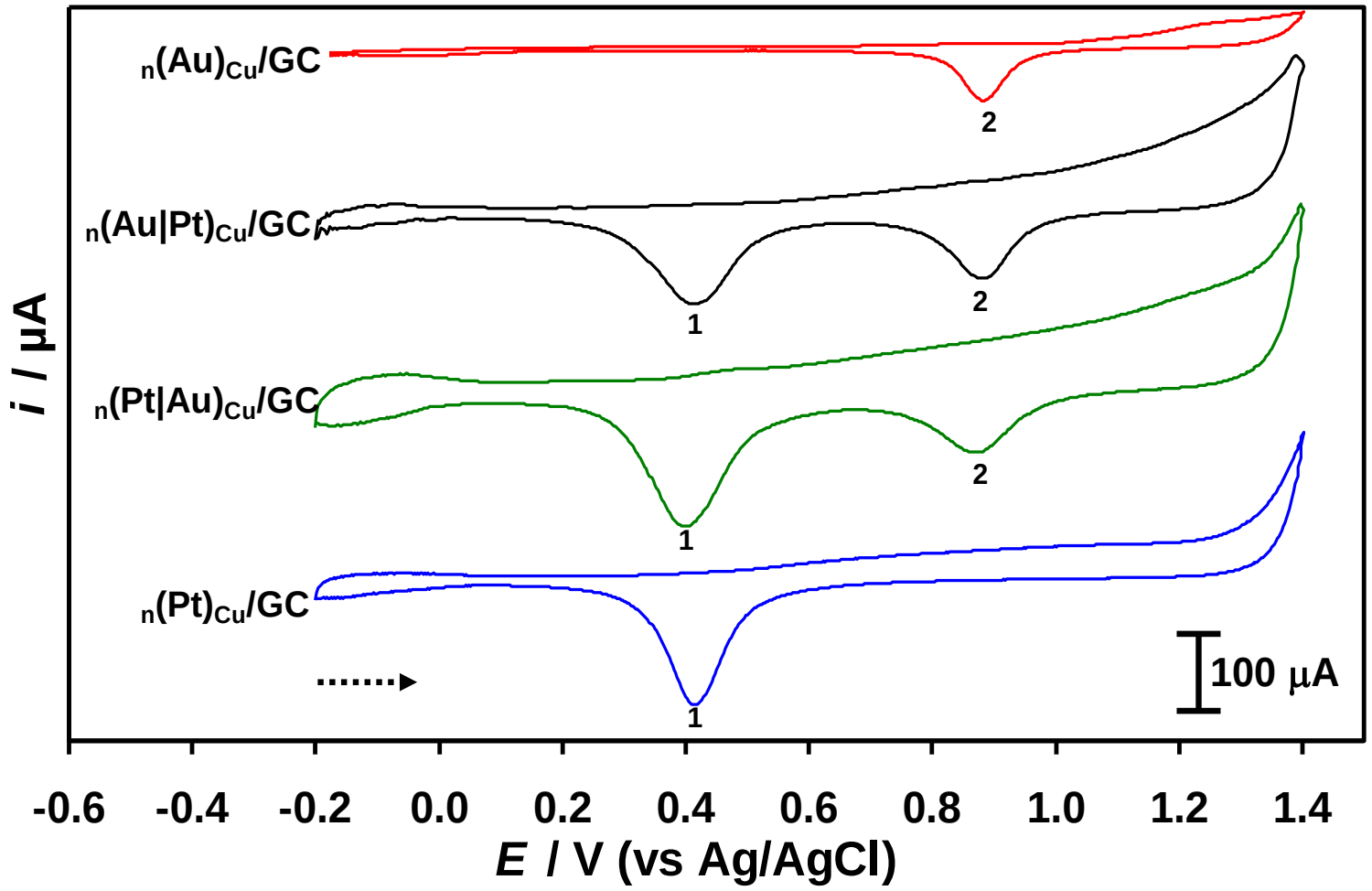
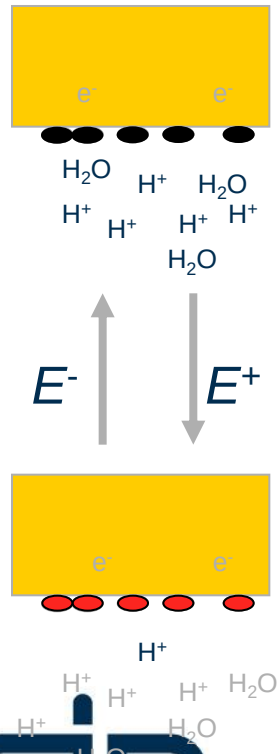
Surface Electrochemistry



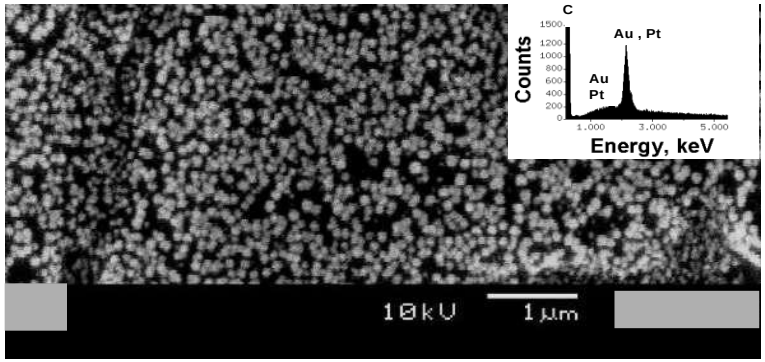


1. PtO_x + ne- + $H^+ \leftrightarrow$ Pt(s) + H_2O

2. AuO_x + H^+ + *n*e– $\leftrightarrow$ Au(s) + H_2O

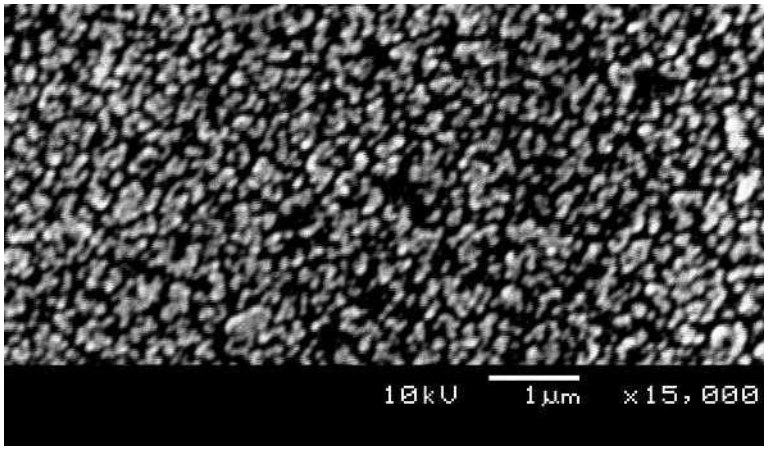
Electrolyte : 0.1 M $HClO_4$ (N_2-saturated)

Surface and Bulk Characterisation – SEM, EDS



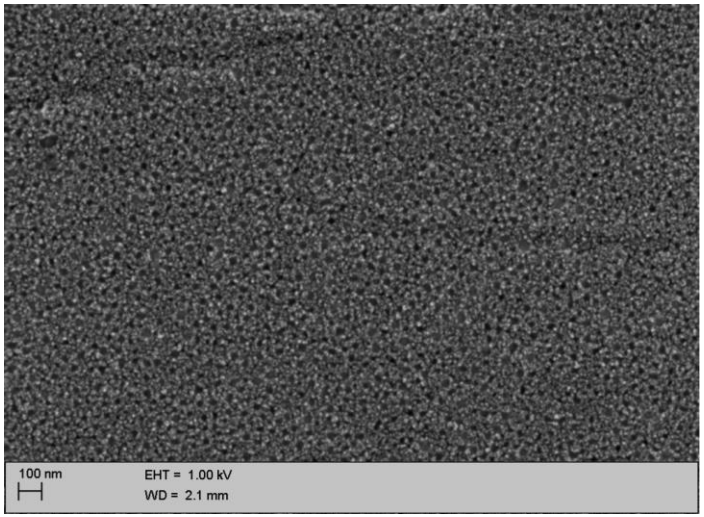
$_{n}(Au|Pt)_{Cu}/GC$

Sequential SLRR deposition



$_{n}(Ru\text{-}Pt)/GC$

Electrochemical codeposition



$_{n}(Ru|Pt)_{Cu,UPD}/Au$

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Electrocatalysis: Methanol Oxidation

$$Pt + CH_3OH \rightarrow Pt-(CH_3OH)_{ads}$$

$$Pt-(CH_3OH)_{ads} \rightarrow Pt-(CO)_{ads} + 4H^+ + 4e^-$$

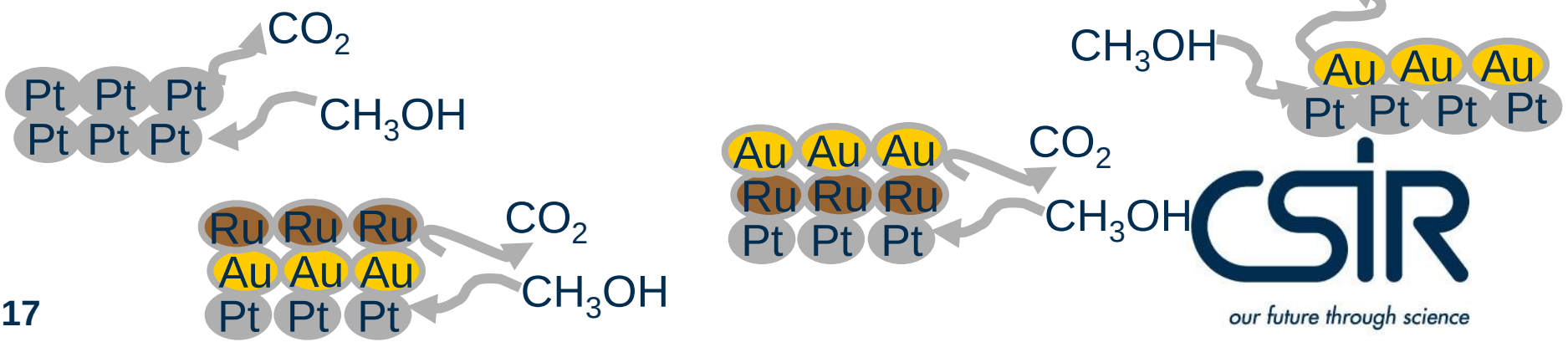
$$H_2O + M \rightarrow M-OH_{ads} + H^+ + e^-$$

$$H_2O + Pt \rightarrow Pt-OH_{ads} + H^+ + e^-$$

$$Pt-CO_{ads} + M-OH_{ads} \rightarrow Pt + M + CO_2 + H^+ + e^-$$

$$Pt-CO_{ads} + Pt-OH_{ads} \rightarrow 2Pt + CO_2 + H^+ + e^-$$

(M = Ru or Au)



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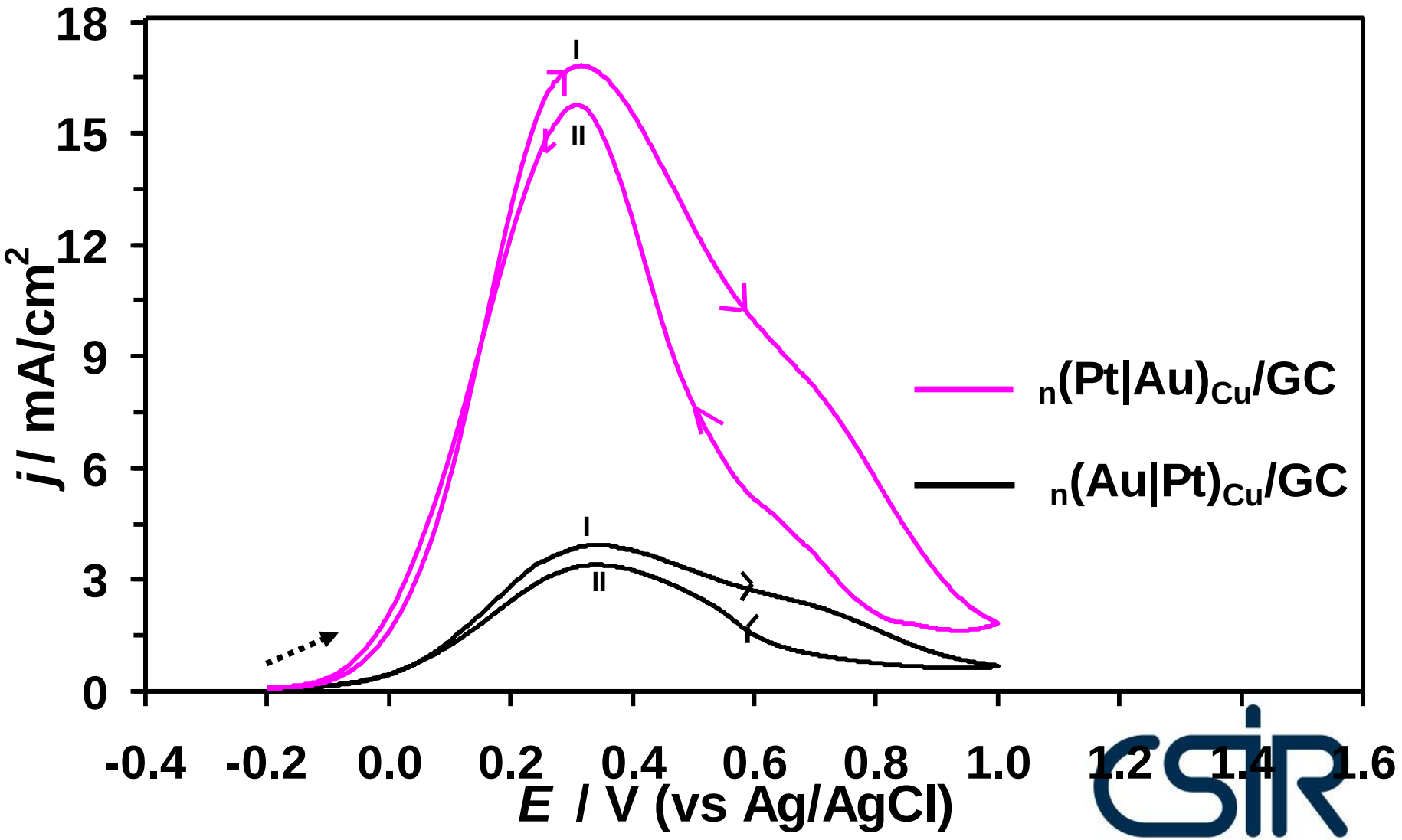
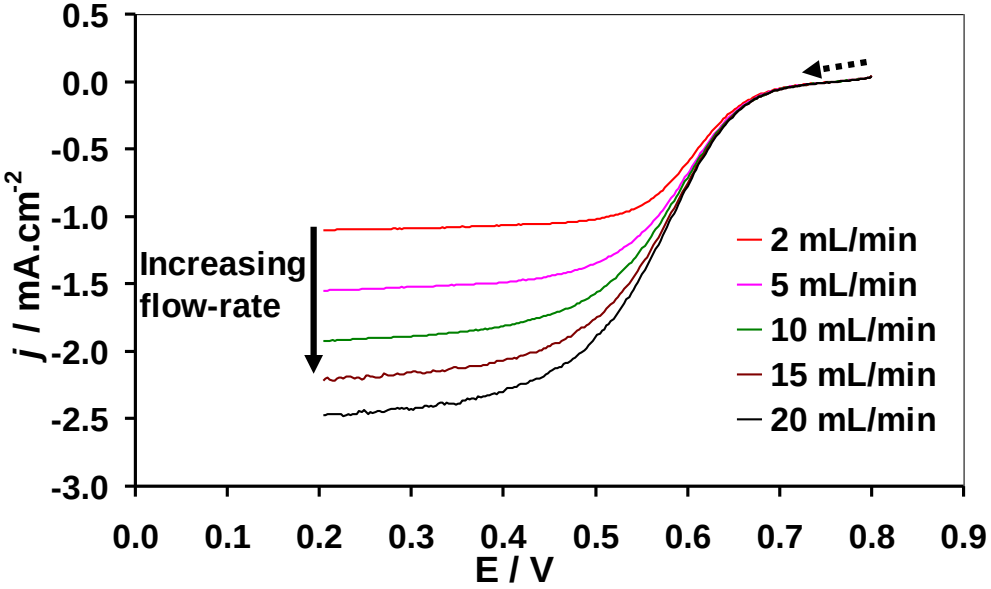
Formic Acid Oxidation



Oxygen reduction



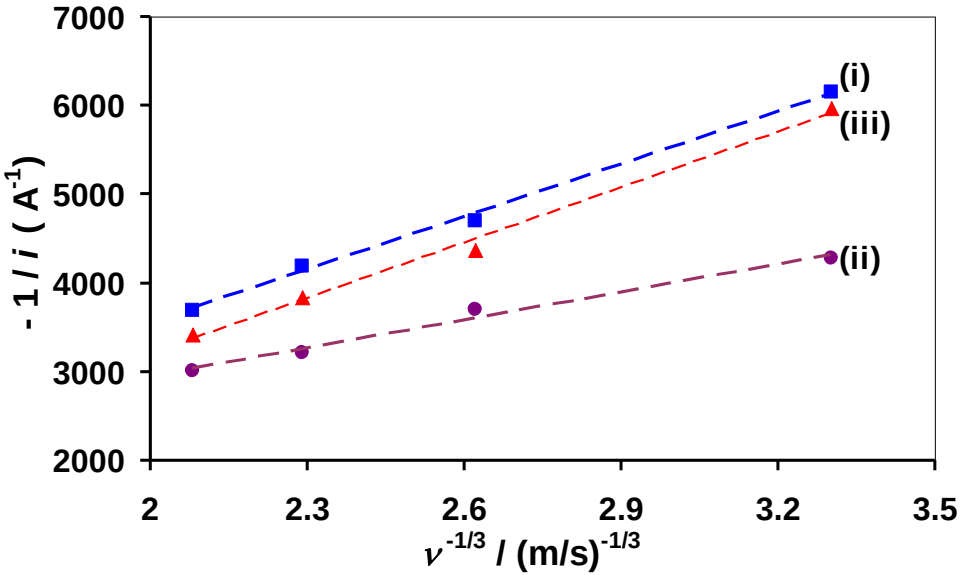
O_2-saturated 0.1 $MHClO_4$

$O_2 + 4H^+ + 4e = H_2O$

Monometallic Pt
Bimetallic Au|Pt

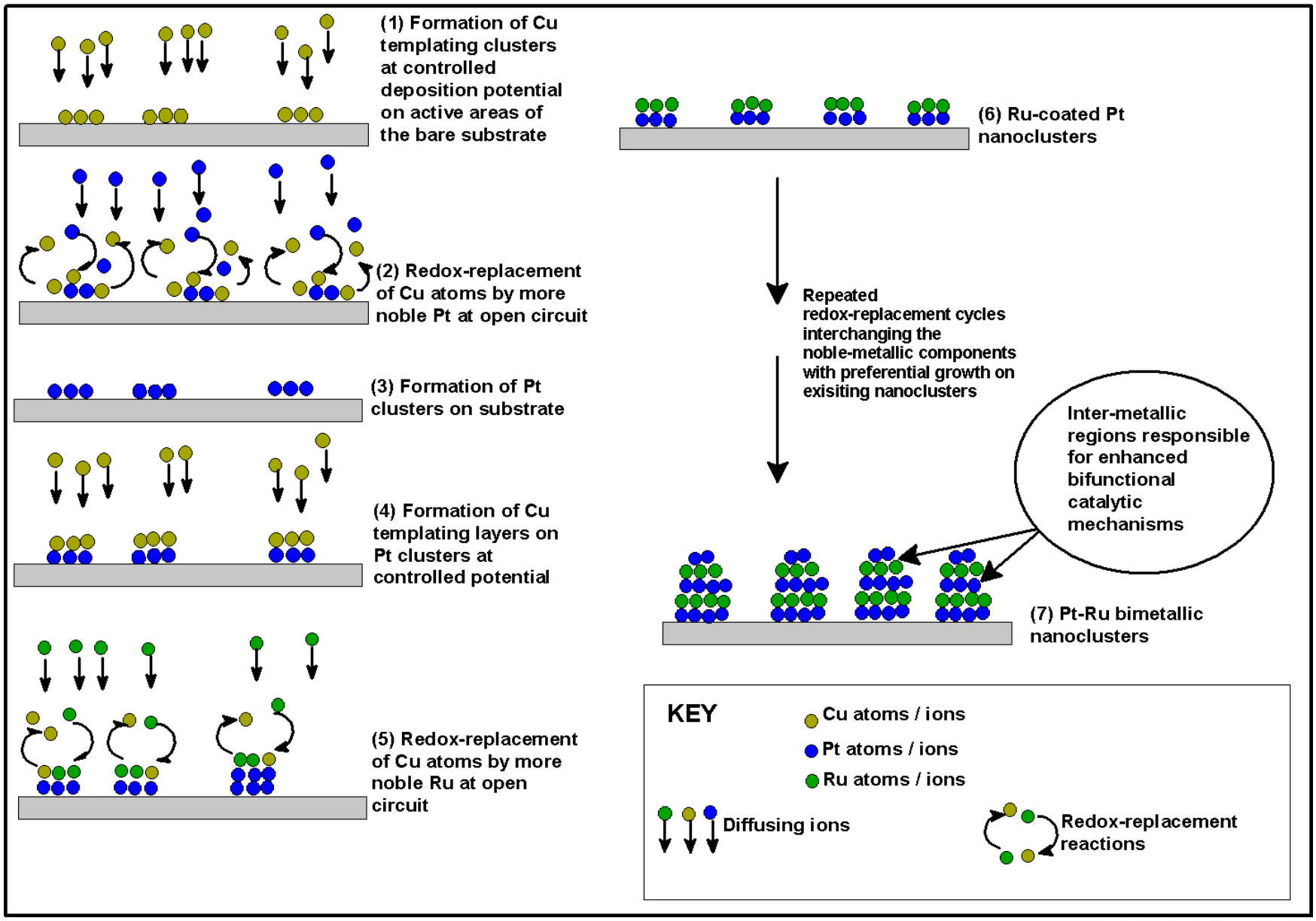
$O_2 + 2H^+ + 2e = H_2O_2$

Bimetallic Ru|Pt



i. $_n(Ru|Pt)_{Cu}/GC$
ii. $_n(Pt)_{Cu}/GC$
iii. $_n(Ru\text{-}Pt)_{Cu}/GC$
n = 8

Conclusions



Conclusions

- The use of stepwise fabrication SLRR reactions at open-circuit results in:
  - more active electrocatalysts,
  - smaller particle sizes,
  - metallic forms generally form, and promotion of bifunctional mechanisms.

- SLRR reactions implemented with codeposition of noble-metal particles generally lead to: Multi-stage electrodeposition

- Multi-stage electrodeposition reactions can be useful in tuning electrocatalytic properties

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