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

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Overview

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

• Tumaini Mkwizu, MSM, CSIR and University of Pretoria, South Africa
• Dr. Mmalewane Modibedi, MSM, CSIR, South Africa
• Prof. Ignacy Cukrowski, University of Pretoria, South Africa
• Prof. John Stickney, University of Georgia, USA
• National Centre for Nano-Structured Materials, MSM, CSIR, South Africa
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

Electrocatalyst particles have to maintain electronic contact with support
Chemical routes to Nanoparticulate Multimetallic Electro catalysts

Electrochemical deposition

Transfer To Electrode

Chemical Reduction / Precipitation

Reducing agent

Metal salts/precursors

Metal salts/precursors
Flow-cell setup

- Ag/AgCl Reference Electrode (RE)
- Stainless Steel Counter Electrode (CE)
- Nut & bolt
- Perspex block for CE and RE
- Inlet to flow-channel
- Silicon Rubber Gasket
- Perspex block for substrate
- Substrate / Working Electrode (WE)
- Outlet from flow-channel
- PTFE substrate holder
- Copper Tape (Connection to Potentiostat’s WE input)
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 $E >> E_{Cu-Cu^{2+}}$

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

3. Inject H$_2$PtCl$_6$ 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 $E >> E_{Cu-Cu^{2+}}$

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

Noble-Metals studied = Pt, Ru, Au, Pd
Substrates = Carbon materials, Gold films
Example of Pulsed-Electrodeposition
Maximum open circuit potential trends

A: Pt|Au/GC

B: Ru|Pt/GC

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

1. $\text{PtO}_x + n\text{e}^- + H^+ \leftrightarrow \text{Pt(s)} + H_2O$

2. $\text{AuO}_x + H^+ + n\text{e}^- \leftrightarrow \text{Au(s)} + H_2O$

Electrolyte : 0.1 M HClO$_4$ (N$_2$-saturated)
Surface and Bulk Characterisation – SEM, EDS

$n(Au\mid Pt)_Cu/GC$
Sequential SLRR deposition

$n(Ru-Pt)/GC$
Electrochemical codeposition

$n(Ru\mid Pt)_{Cu,UPD}/Au$
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)
Formic Acid Oxidation

$J$ / mA/cm$^2$

$E$ / V (vs Ag/AgCl)

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

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

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Oxygen reduction

\[ \text{O}_2 + 4\text{H}^+ + 4\text{e} = \text{H}_2\text{O} \]

Monometallic Pt

\[ \text{O}_2 + 2\text{H}^+ + 2\text{e} = \text{H}_2\text{O}_2 \]

Bimetallic Au|Pt

Bimetallic Ru|Pt

\[ \text{O}_2 \text{-saturated} \ 0.1 \text{M} \text{HClO}_4 \]

Increasing flow-rate

**Graph:**

- 2 mL/min
- 5 mL/min
- 10 mL/min
- 15 mL/min
- 20 mL/min

**Table:**

- i. \( n(\text{Ru}\vert\text{Pt})_{\text{Cu}/\text{GC}} \)
- ii. \( n(\text{Pt})_{\text{Cu}/\text{GC}} \)
- iii. \( n(\text{Ru}-\text{Pt})_{\text{Cu}/\text{GC}} \)

\( n = 8 \)
Conclusions

1. Formation of Cu templating clusters at controlled deposition potential on active areas of the bare substrate.

2. Redox-replacement of Cu atoms by more noble Pt at open circuit.

3. Formation of Pt clusters on substrate.

4. Formation of Cu templating layers on Pt clusters at controlled potential.

5. Redox-replacement of Cu atoms by more noble Ru at open circuit.

6. Ru-coated Pt nanoclusters.

7. Pt-Ru bimetallic nanoclusters.

Inter-metallic regions responsible for enhanced bifunctional catalytic mechanisms.

KEY:
- **Cu atoms / ions**
- **Pt atoms / ions**
- **Ru atoms / ions**
- **Diffusing ions**
- **Redox-replacement reactions**
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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Thank You