Crystalline Thin Films: The Electrochemical Atomic Layer Deposition (ECALD) view

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Outline

- Acknowledgements
- Context: Crystalline Thin films
- What is ECALD?
    - Mechanism
- Instrumental set-up
- Applications
  - Electrocatalysis
    - Deposition on various substrates: work done @ EaP
  - Compound semiconductor
- Conclusions

Acknowledgements

- Dr. Tumaini Mkwizu, PhD work on ECALD
- Ms. Nikiwe Kunjuzwa, PhD student- ECALD and batteries
- Prof. Kenneth Ozoemena, Research group leader and electrochemist
- Dr Mkhulu Mathe, Competence area manager, electrochemist and ECALD expert

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Crystalline Thin Films

- Application
  - Historical: light absorber material
    CdTe, crystalline Si

  - Modern: light absorber material – Solar cells
    Cu, In, Ga, Se (CIGS)- developed by Vivian Alberts and UJ
  - low material cost in 2011- potentially low fabrication costs

- Growth methodologies
  - Molecular beam epitaxy/ chemical vapour deposition
    Disadvantages: expensive equipment, use toxic precursors, Vacuum and High Temperature

  - Electrochemical methods: co-deposition, precipitation
    Disadvantages: lack of control during deposition

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What is ECALD?

- Definition:

alternated electrodeposition of atomic layers of elements on a substrate, employing under-potential deposition (UPD) in which one element deposits onto another element at a voltage prior to that necessary to deposit the element onto itself.

- Advantages:
    - ambient temperature,
    - use small concentrations of precursor solutions,
    - optimized solutions and potential separately

Offers atomic layer control- fundamental for controlled growth processes

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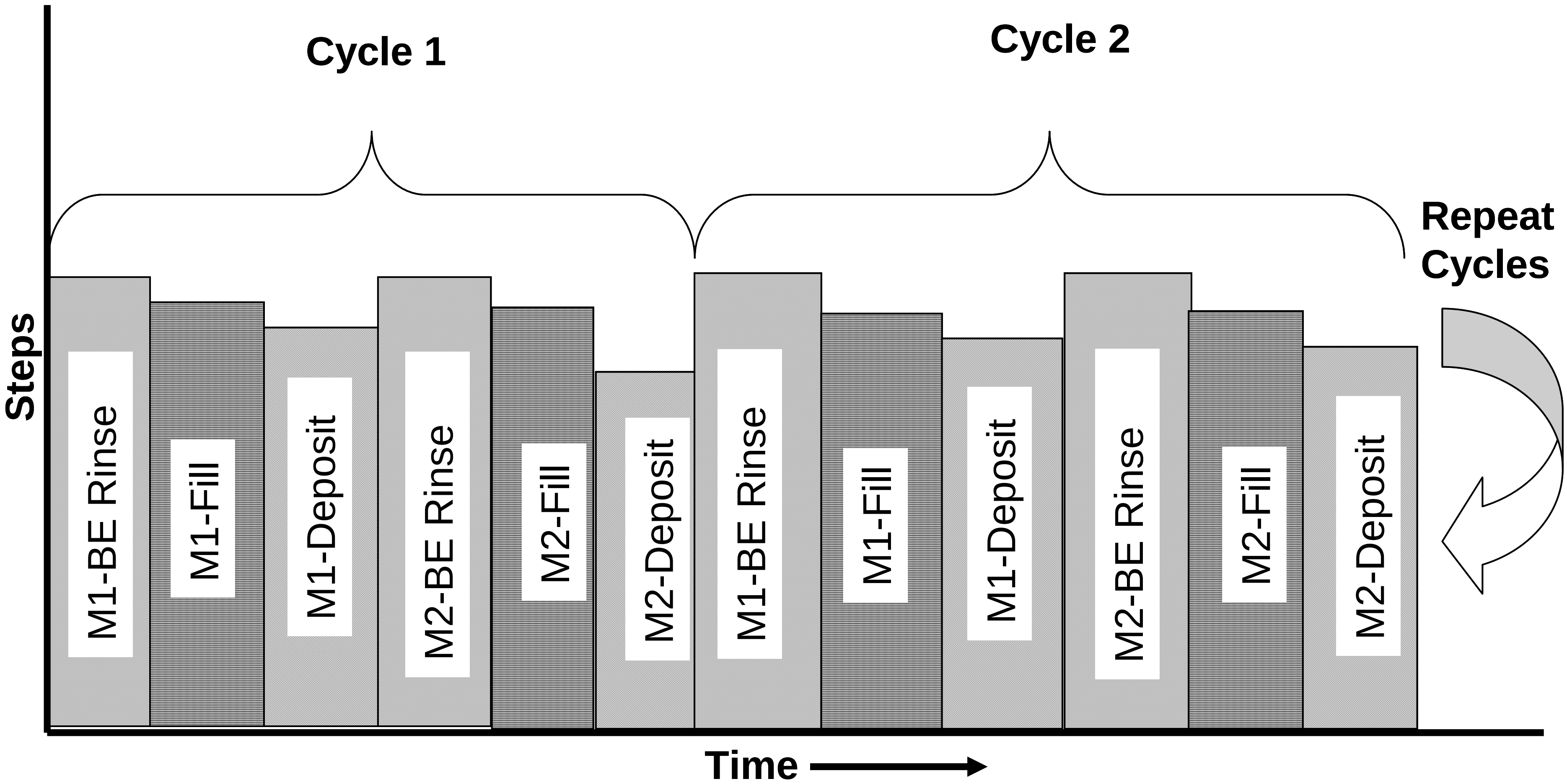
Mechanism-Sequential deposition



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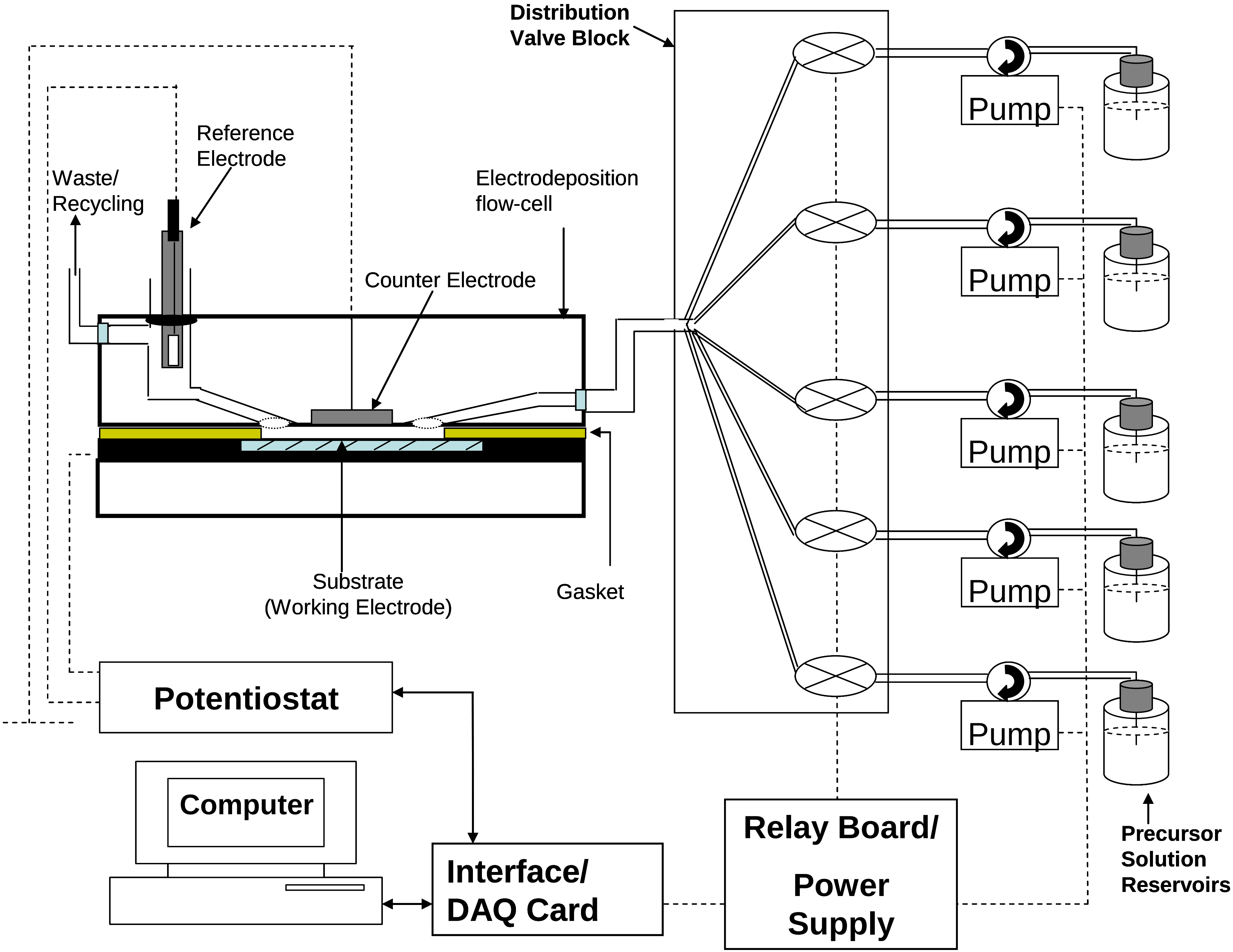
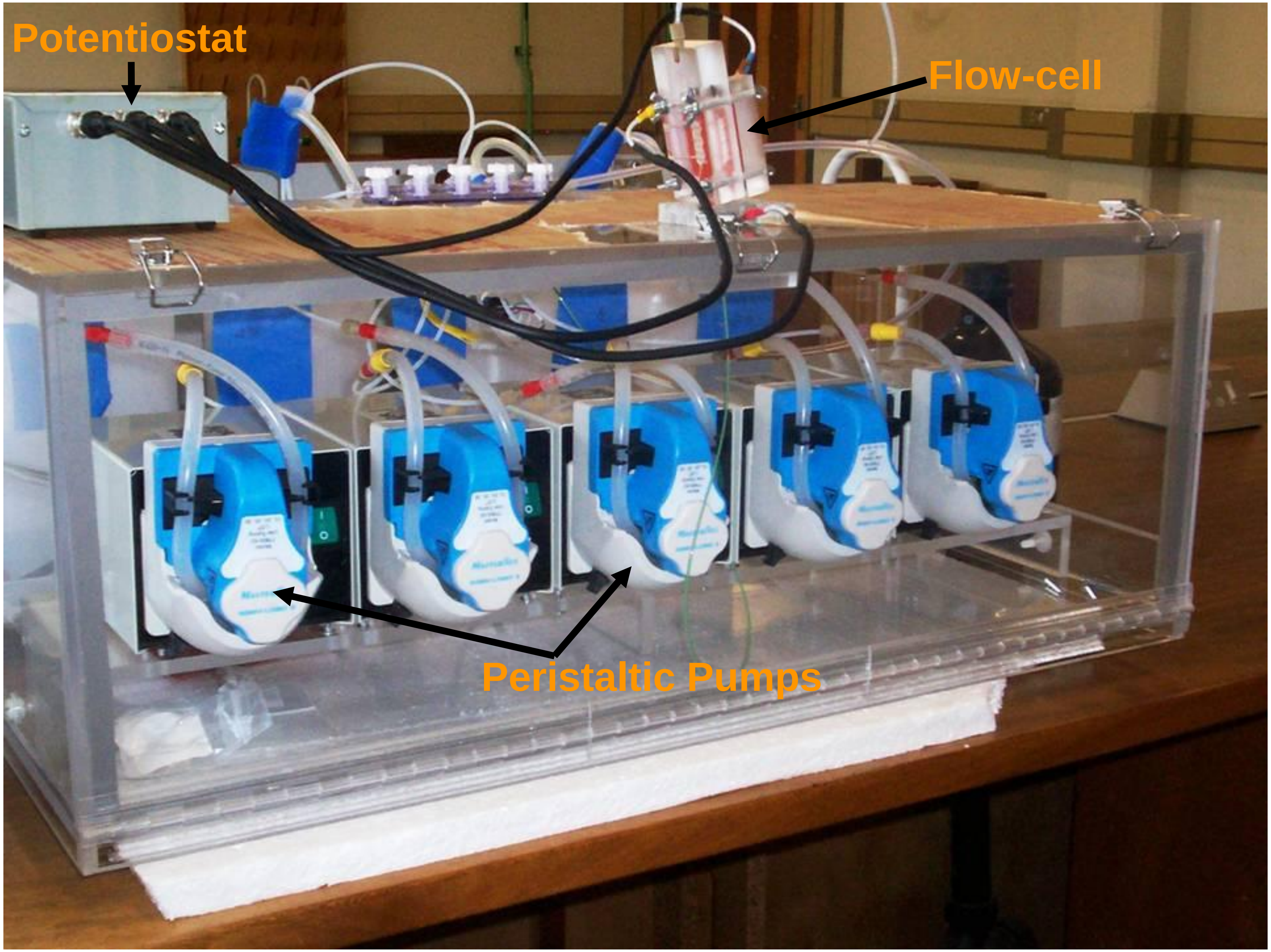


Distribution Valve Block
Reference Electrode
Waste/ Recycling
Electrodeposition flow-cell
Counter Electrode
Substrate (Working Electrode)
Gasket
Pump
Pump
Pump
Pump
Pump
Potentiostat
Computer
Interface/ DAQ Card
Relay Board/ Power Supply
Precursor Solution Reservoirs



Instrumental set-up – Pumping system, Potentiostat and Flow-Cell Connectivity

APPLICATIONS

- Electrocatalysis

Noble-Metals studied = Pt, Ru, Au, Pd
Substrates = Carbon materials-fuel cell carbon paper, Gold films

T.S.Mkwizu, M.K. Mathe, and I. Cukrowski, ECS Transactions, Vol.19, 97-113 (2009)
T.S.Mkwizu, M.K. Mathe, and I. Cukrowski, Langmuir, Vol. 26, 570 - 580 (2010)
T.S Mkwizu, M.R. Modibedi, and M. K. Mathe, 219th ECS Meeting (2011)

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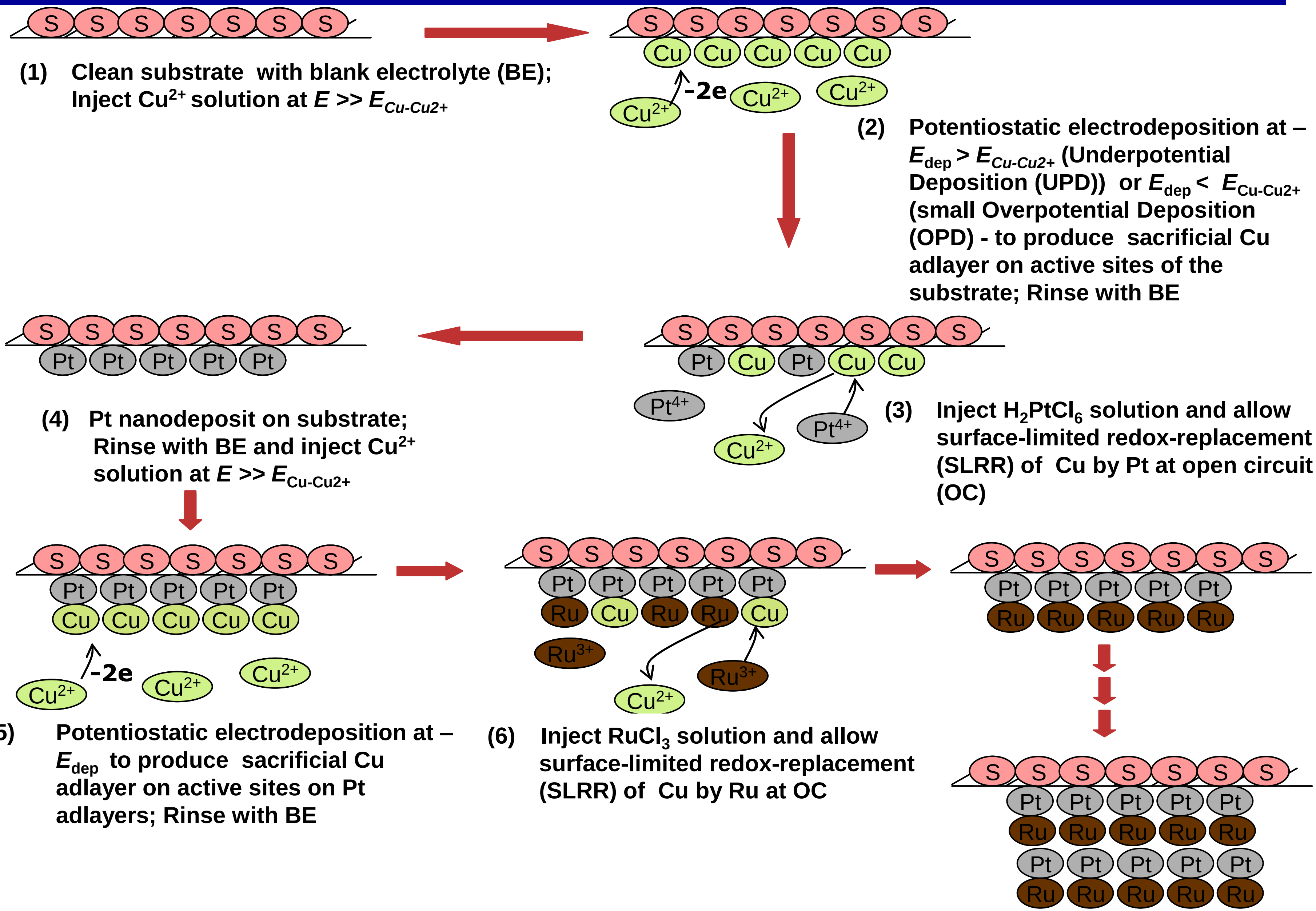
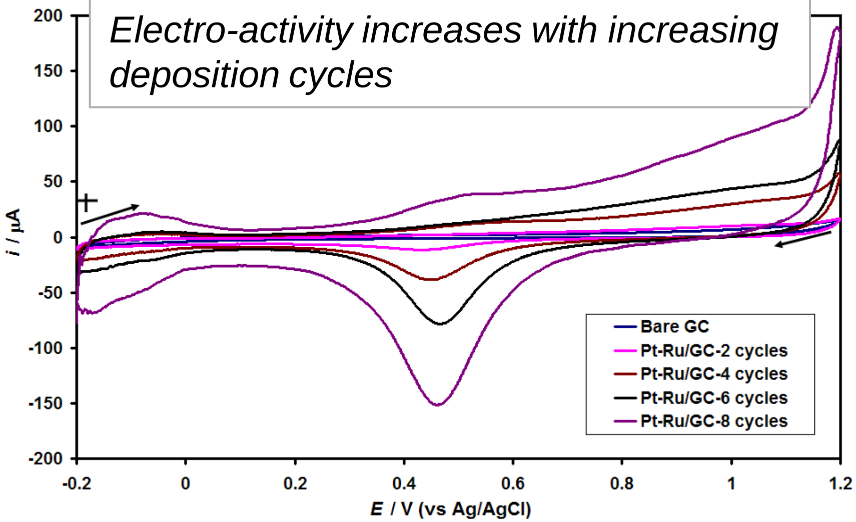
Sequential electrodeposition coupled to Surface-limited Redox-replacement reactions: Synthesis of multilayered bimetallic RuPt electrocatalyst

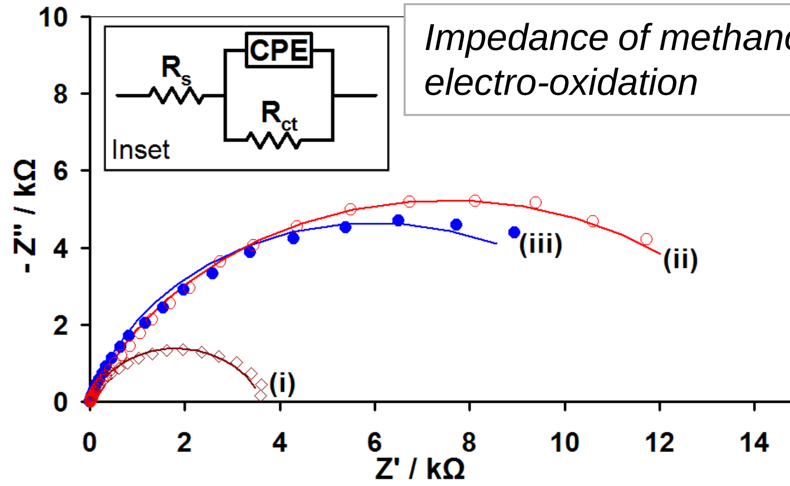


Tuning Electrocatalysis: Electrochemical Characterisation

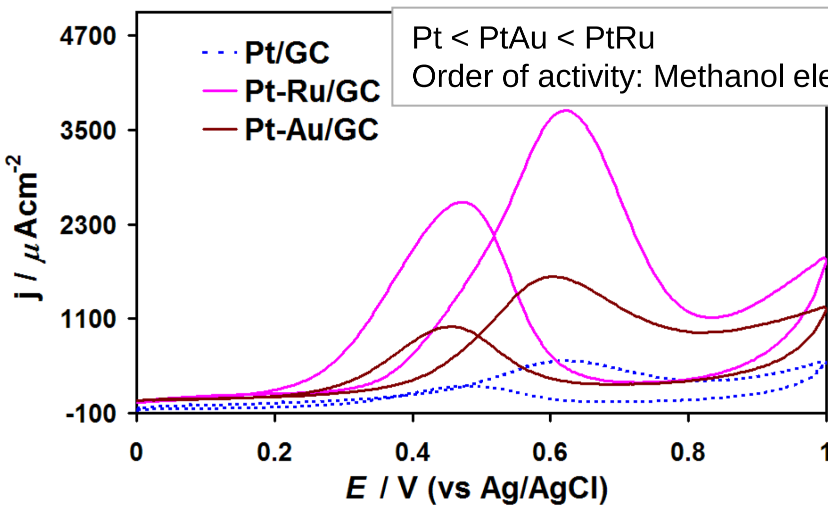
Electro-activity increases with increasing deposition cycles



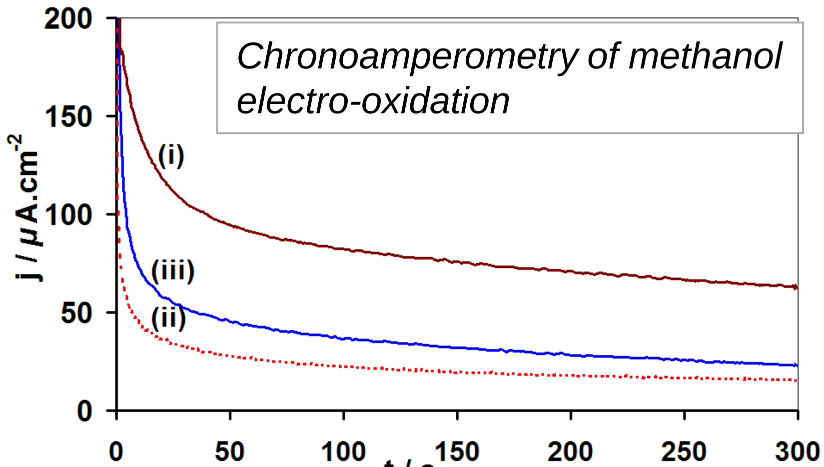
Impedance of methanol electro-oxidation



Pt < PtAu < PtRu
Order of activity: Methanol electro-oxidation



Chronoamperometry of methanol electro-oxidation

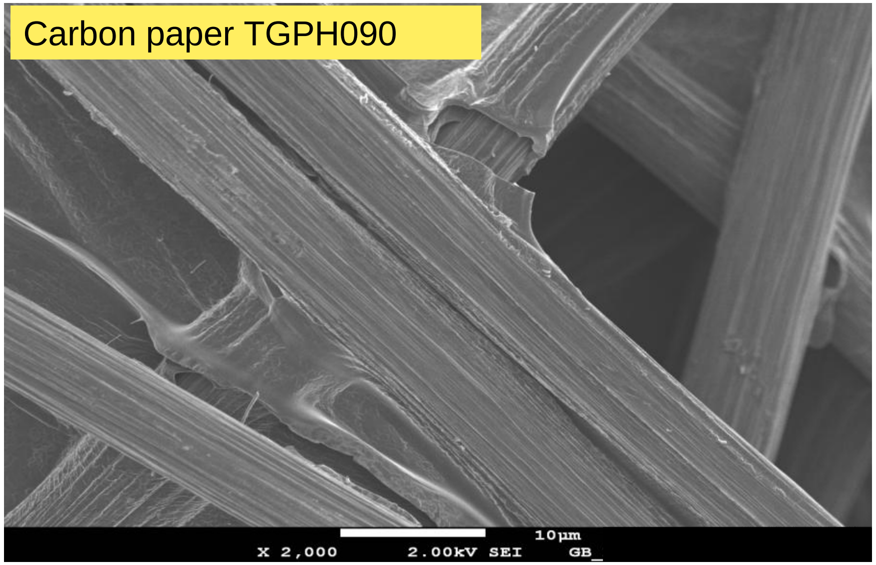


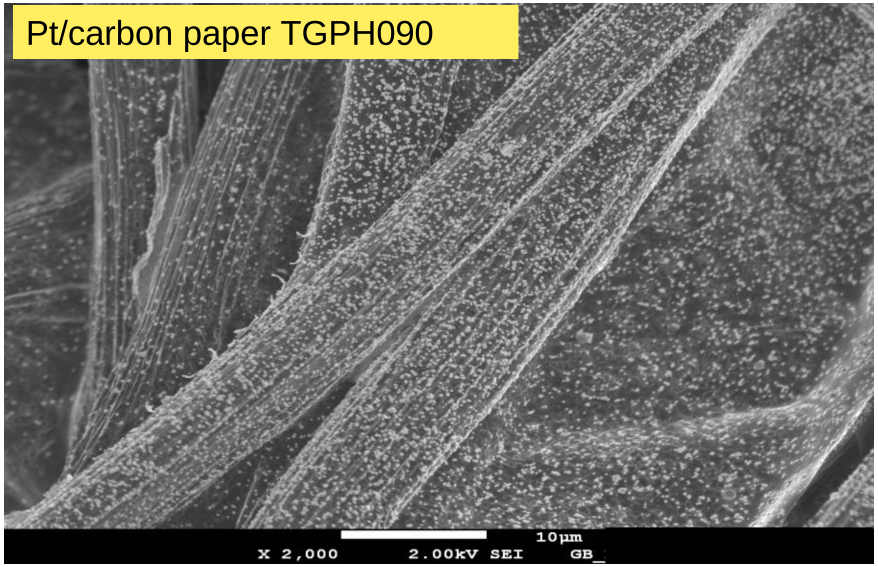
(i) Sequentially-deposited with Cu SLRR bimetallic PtRu / GC
(ii) Sequentially- *codeposited* with Cu SLRR bimetallic Pt-Ru/GC
(iii) Sequentially-deposited with Cu SLRR monometallic Pt/GC

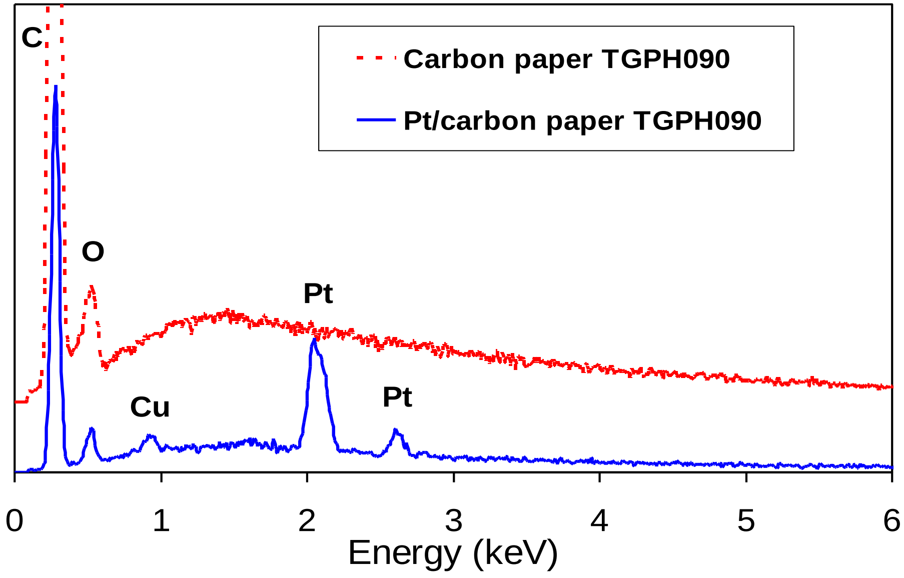
0.1M $HClO_4$ + 0.5 M CH_3OH

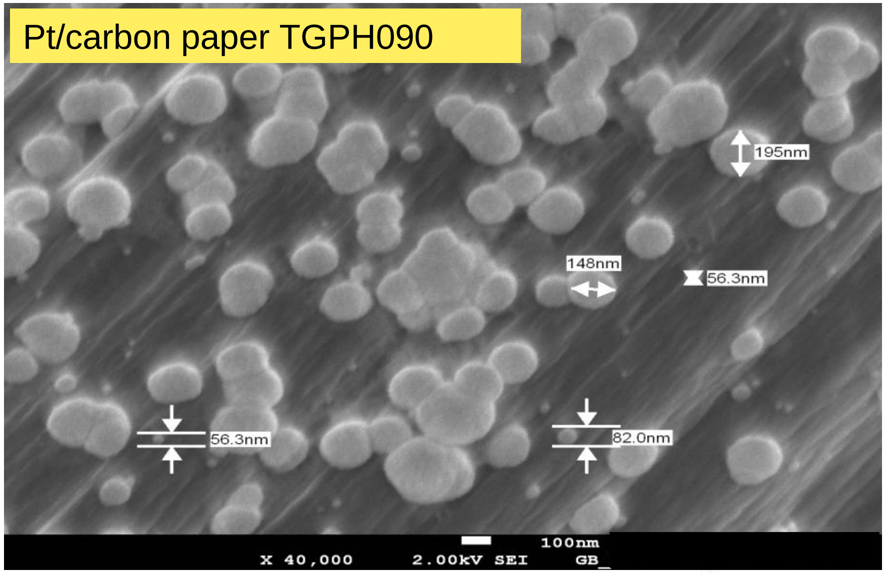
T.S.Mkwizu, M.K. Mathe, and I. Cukrowski, ECS Transactions, Vol.19, 97-113 (2009)
T.S.Mkwizu, M.K. Mathe, and I. Cukrowski, Langmuir, Vol. 26, 570 - 580 (2010)

Tuning Electrocatalysis on Fuel Cell gas diffusion layer: SEM micrographs and EDX profile

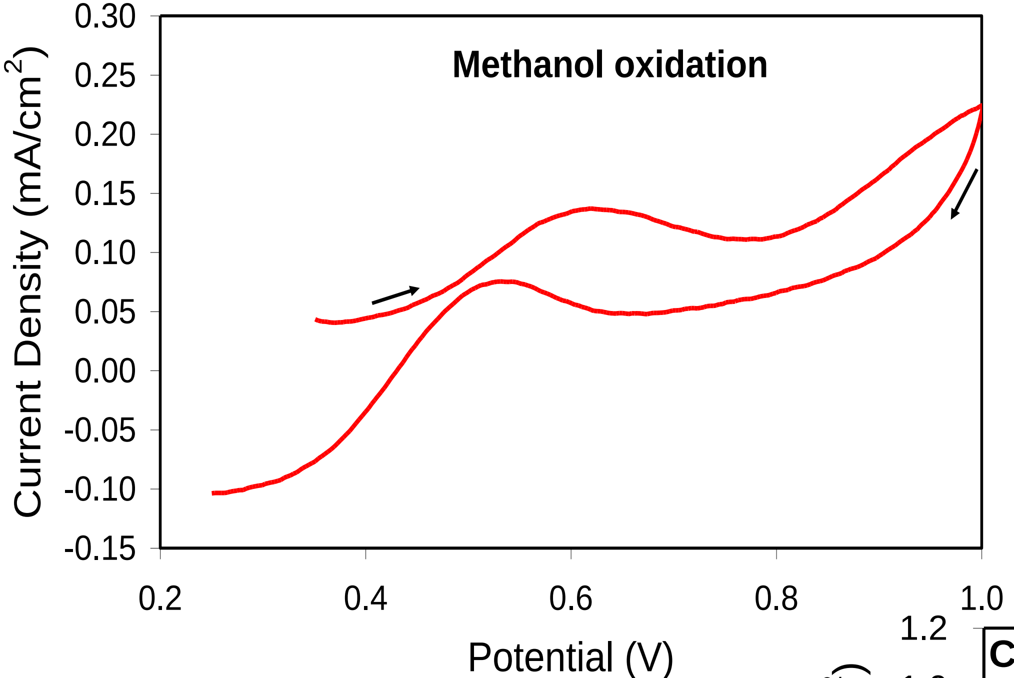








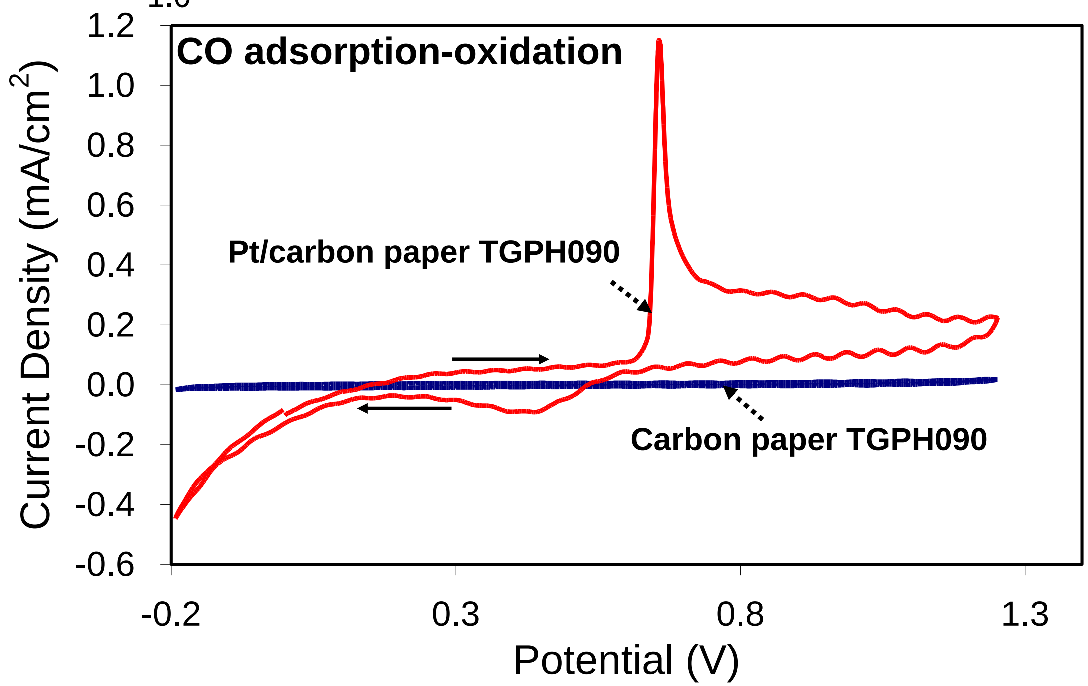
Tuning Electrocatalysis on Fuel Cell gas diffusion layer: Electrochemical Characterisation



Cyclic voltammograms at 50 mV/s in

(i) 0.1 M $HClO_4$ + 0.1 M Methanol

(ii) 0.1 M $HClO_4$ + CO



• Compound Semiconductors

- **Group II - VI, Group III - V , Group IV - VI: Optoelectronic materials**

  CdTe, CdSe, GaAs, HgSe **-** photovoltaics, photon sensors, lasers etc.

- **Substrates =** Gold, carbon material

  Mkhulu K. Mathe et al. J. Electrochem. Soc., Volume 152, Issue 11, C751-C755 (2005)
  Mkhulu K. Mathe et al. J. Crystal Growth Volume 271, Issues 1-2, 55-64 (2004)

• Energy storage

- **Physical form (capacitors) and Electrochemical form (batteries)**
- **Obstacle to increasing thin film battery storage capacity:** limited diffusion path length of ions and electrons
- **Solution: area enhancement- 3D thin films**
  - Increases total amount of active material while maintaining short diffusion path
  - Results- high power and energy density

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Conclusions

- ECALD:
  - controlled growth of thin film deposits
  - atomic layer control is key to reducing the amount of PEMFC catalysts
  - possibility of a 3D battery stack

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Thank You

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