# *Pt deposition on Carbon paper and Ti mesh substrates by Surface Limited Redox Replacement*

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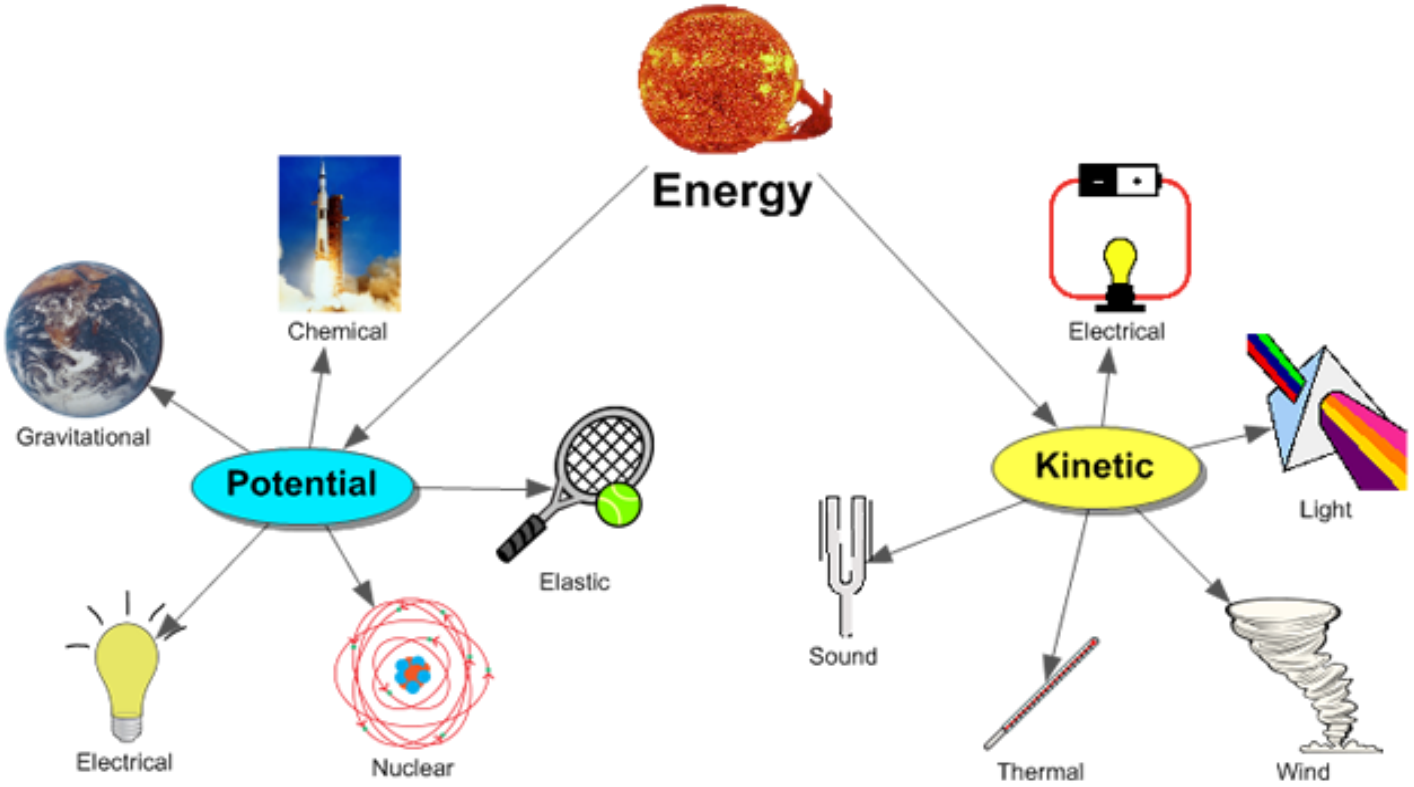
# Outline

- Rationale
- Electrochemical atomic layer deposition technique (ECALD)
- Characterization and Electrochemical Evaluation of Pt
  - on Carbon paper
  - on Ti mesh
- Concluding remarks and future work
- Acknowledgements

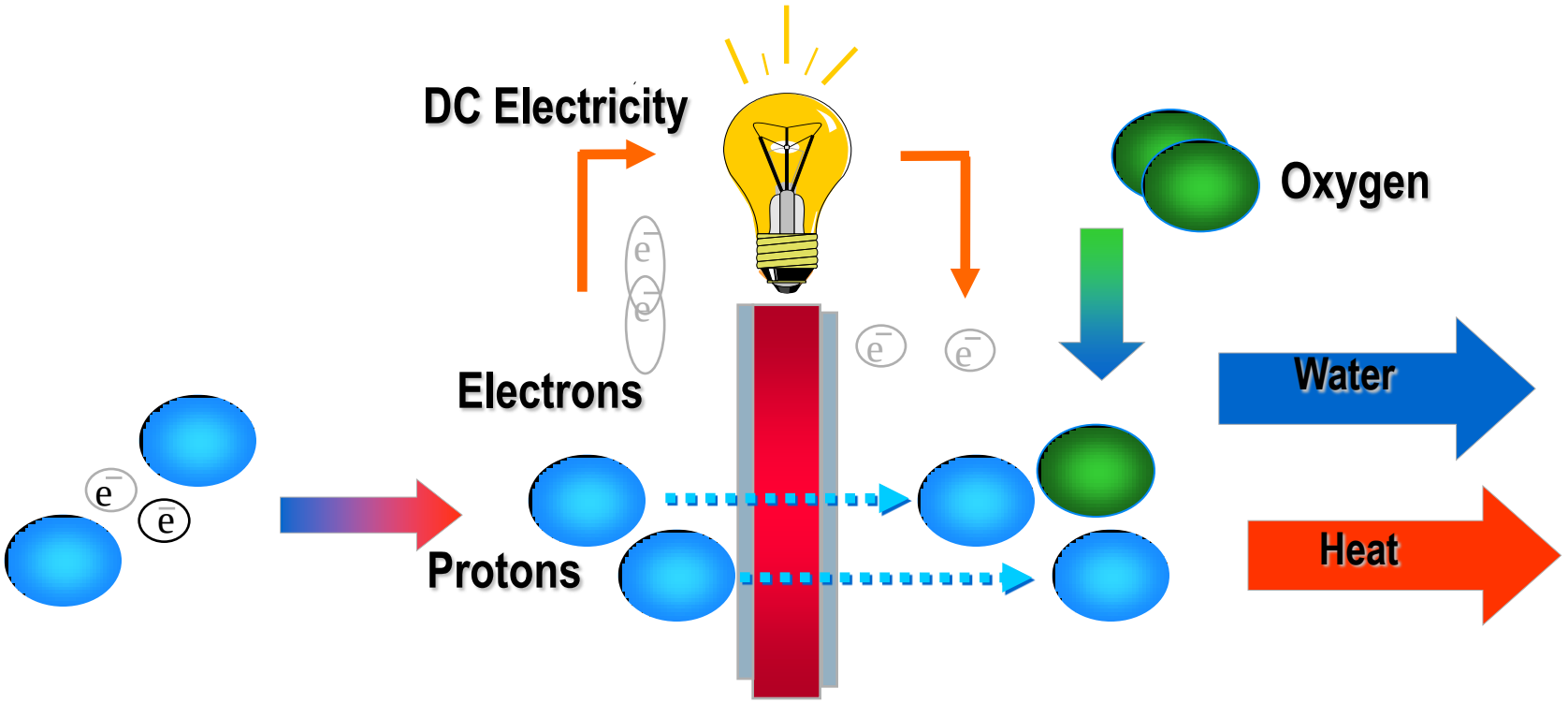
# Rationale

- WORLD WIDE CRISIS:




- Alternative energy resources
  - Fuel cell (FC)

# What is a FC?




$H_2 \leftrightarrow 2H^+ + 2e^-$

0 Volts

$1/2O_2 + 2e^- \leftrightarrow 1/2O_2^{--}$

~1.23 Volts

$H_2 + 1/2O_2 \rightarrow H_2O$

*Approx, 1 volt or less/cell, therefore add cells together*

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# What is a FC? (cont'd)

- Categorized *based on the type of electrolyte* used.

| Fuel Cell Type | Current Density ($mA/cm^2$) | System Efficiency | Fuel Proc. Complexity | Stack Power Density | Transient Capability |
|---|---|---|---|---|---|
| **Alkaline** | 60 - 120 | 35 - 50 | Medium | Medium | High |
| **PAFC** | 100 - 400 | 35 - 45 | Medium | Medium | Medium |
| **MCFC** | 100 - 200 | 45 - 55 | Low | Low | Low |
| **SOFC** | 100 - 300 | 45 - 50 | Low | Medium | Low |
| **PEMFC** | **400 - 900** | **32 - 40** | **High** | **High** | **High** |

- Membrane electrolyte assembly (MEA)
  - Electrolyte is sandwiched between anode and cathode
  - Anode catalyst: fuel oxidation reaction
  - Cathode catalyst: oxygen reduction reaction

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# Some PEMFC challenges

- **Polymer membrane electrolyte:** Drs Nonjola and Zheng's presentations

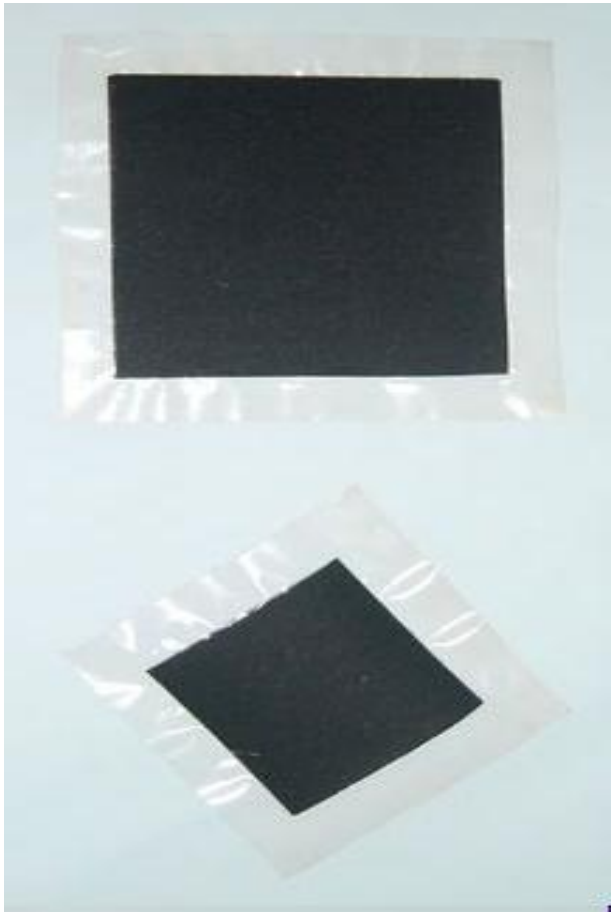
- **Precious metal catalyst- high costs**
  - Lower amount of Pt (< 0.03 mg/cm$^2$)
  - High Pt utilization

- **Carbon support corrosion and Pt dissolution-degradation**
  - Alternative support material-good corrosion resistance

**Key to successful MEA fabrication**

- efficient deposition of the catalysts- resulting in high Pt utilization

- Good contact between membrane, GDL and catalyst layers



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# Why 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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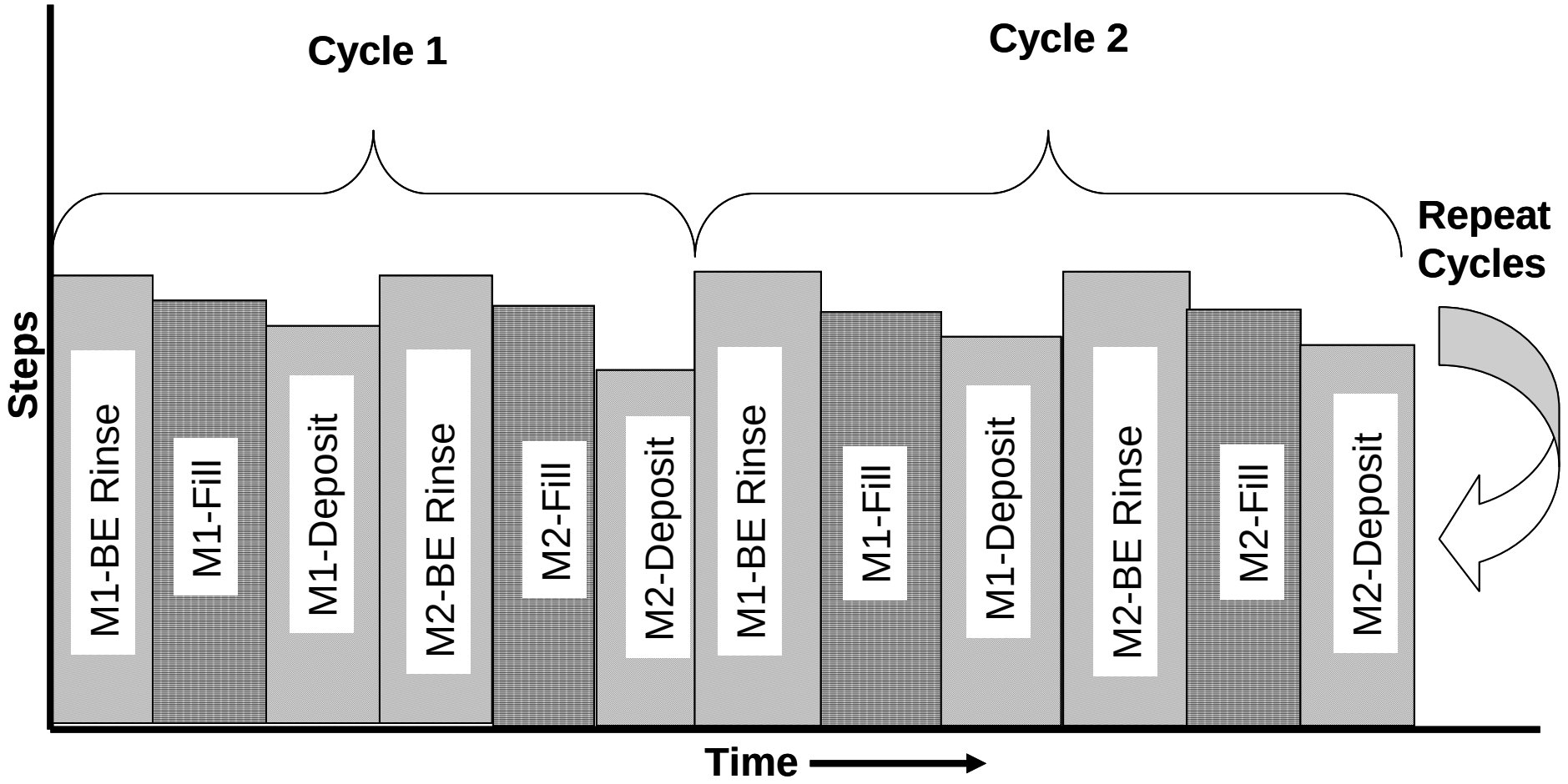
# Mechanism-Sequential deposition




**Noble-Metal: Pt**

**Substrates: Carbon paper, Ti-Mesh**

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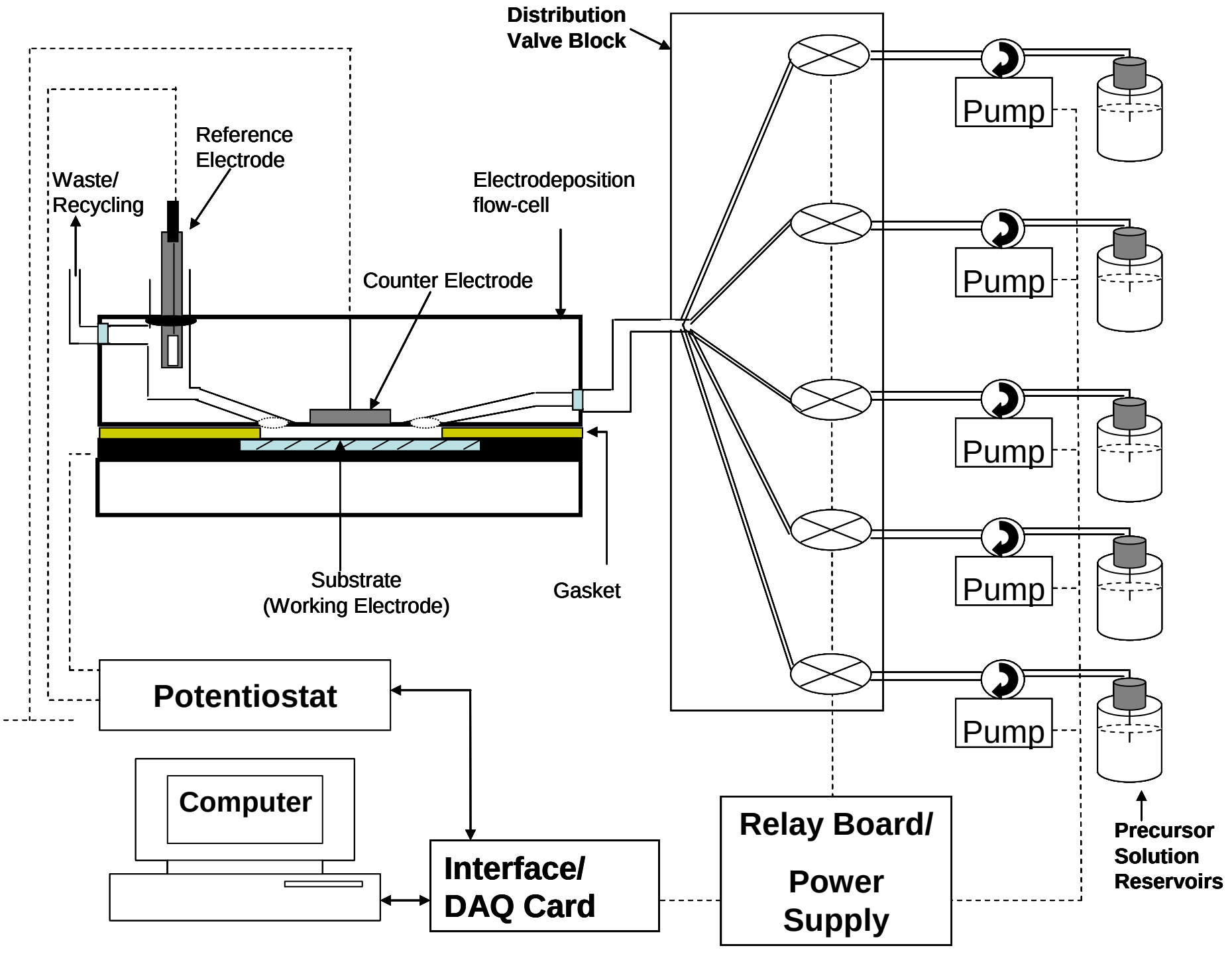
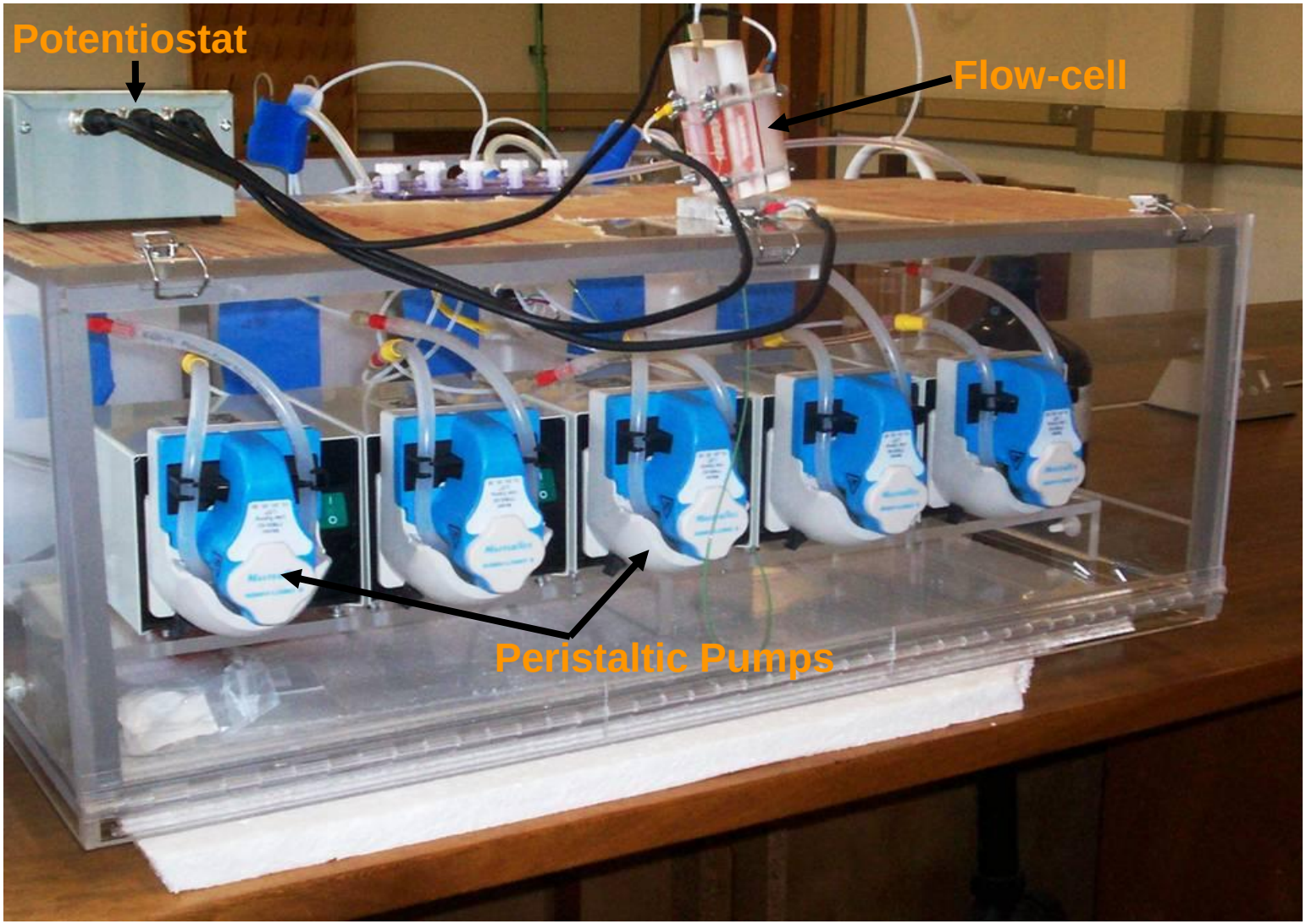

Distribution
Valve Block
Reference
Electrode
Waste/
Recycling
Electrodeposition
flow-cell
Counter Electrode
Substrate
(Working Electrode)
Gasket
Pump
Pump
Pump
Pump
Pump
Potentiostat
Computer
Interface/
DAQ Card
Relay Board/
Power
Supply
Precursor
Solution
Reservoirs




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

*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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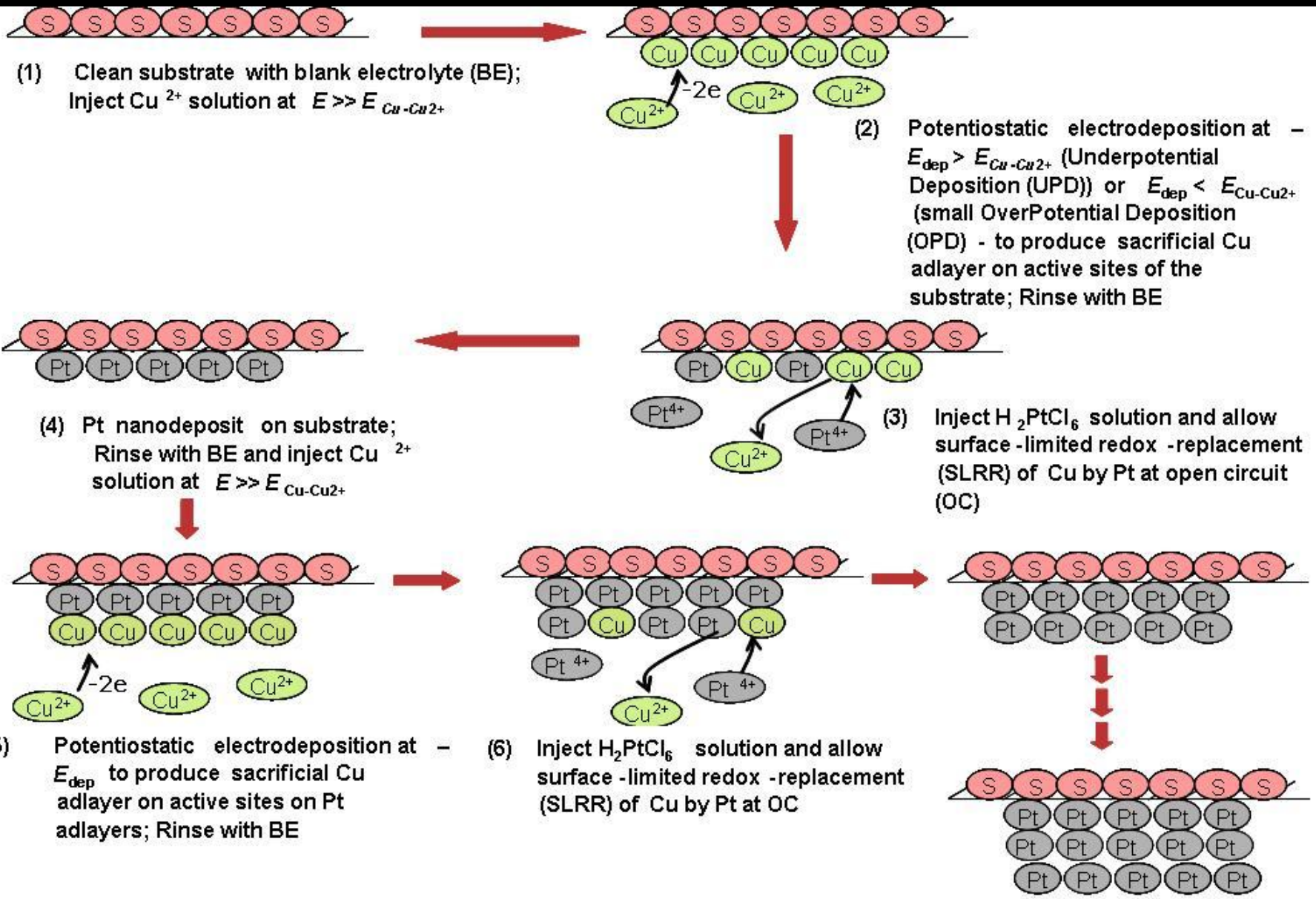
# Sequential electrodeposition coupled to Surface-limited Redox-replacement reactions: Synthesis of multilayered Pt electrocatalyst




(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 $E >> E_{Cu\text{-}Cu2+}$

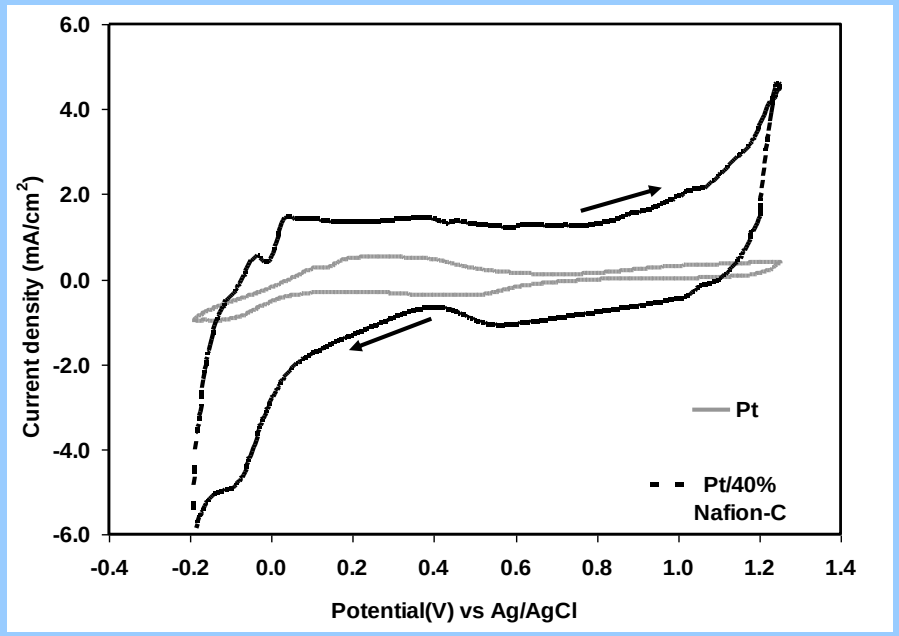
(5) Potentiostatic electrodeposition at – $E_{dep}$ to produce sacrificial Cu adlayer on active sites on Pt adlayers; Rinse with BE

(6) Inject $H_2PtCl_6$ solution and allow surface-limited redox-replacement (SLRR) of Cu by Pt at OC

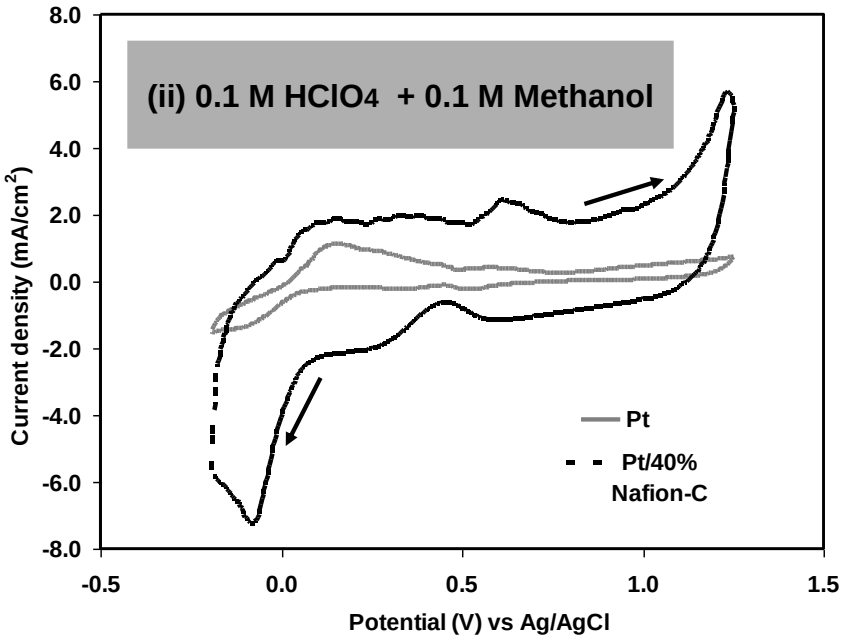
# Pt supported on FC gas diffusion layer: Electrochemical Evaluation

**Cyclic voltammograms at 50 mV/s in**

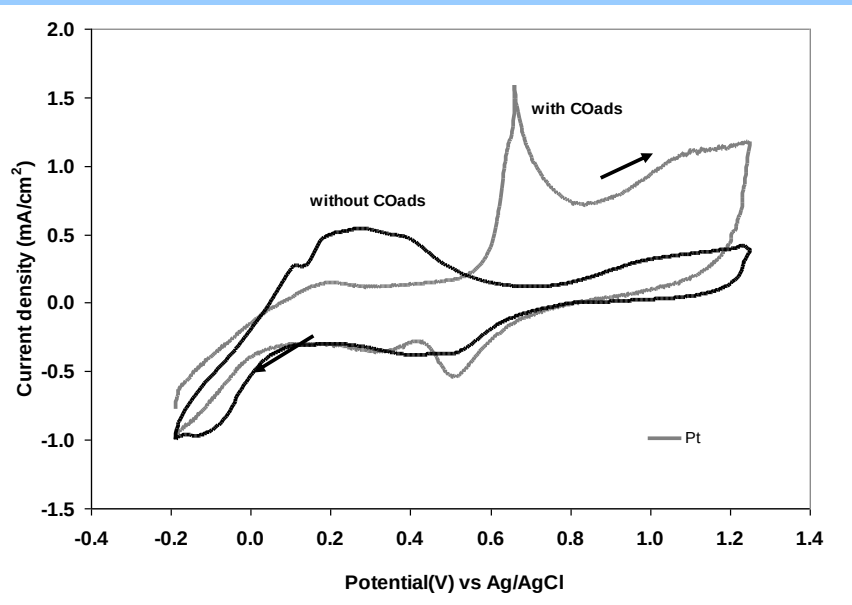
**(i) 0.1 M $HClO_4$**



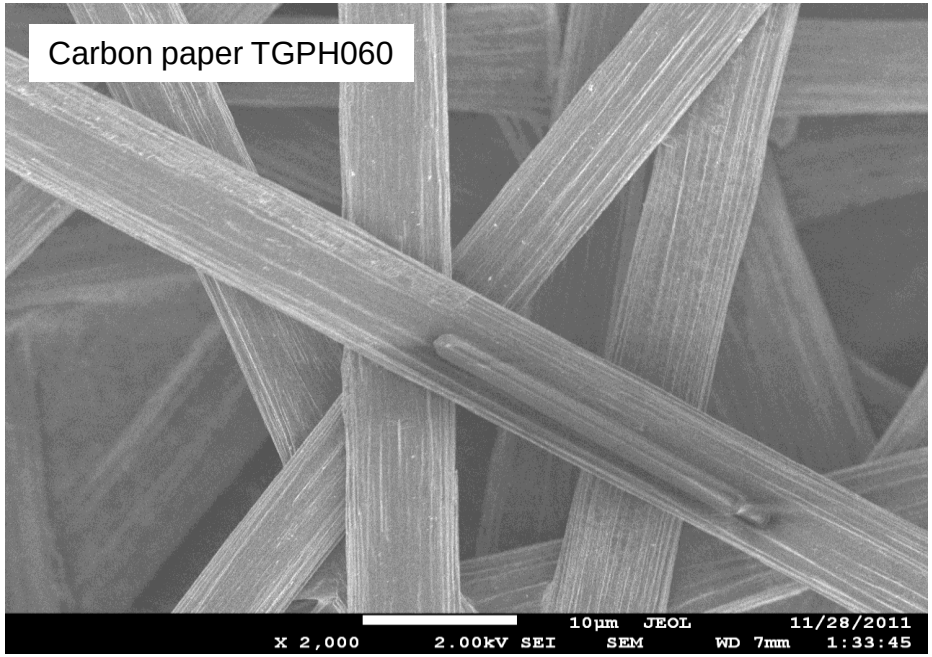

**(ii) 0.1 M $HClO_4$ + 0.1 M Methanol**

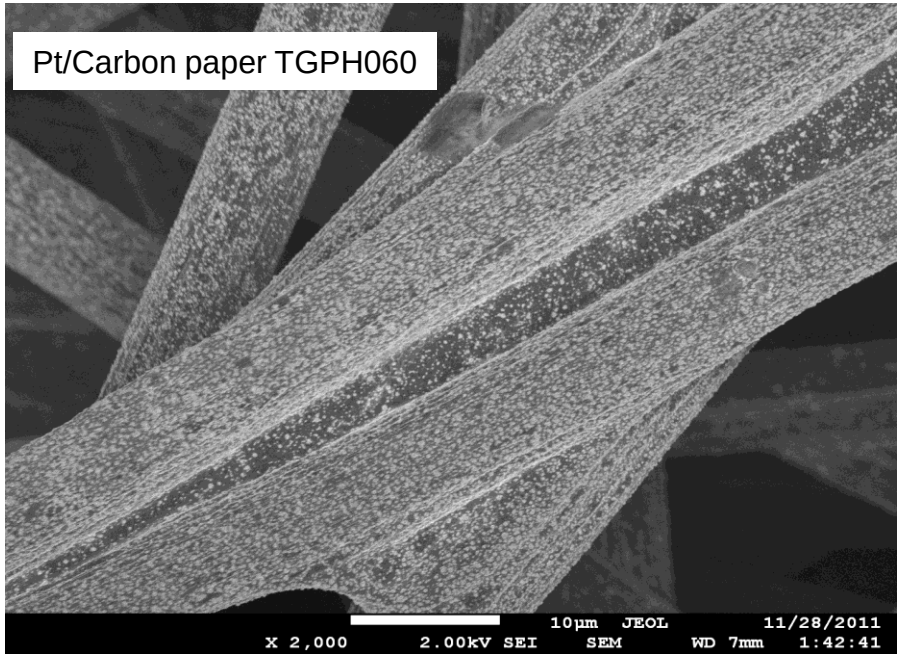


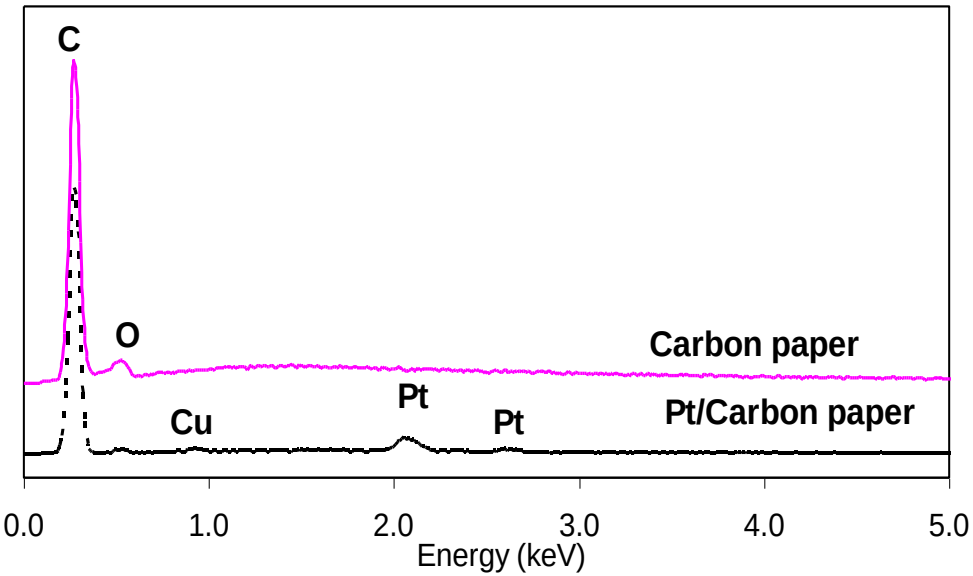

**(iii) 0.1 M $HClO_4$ + CO**

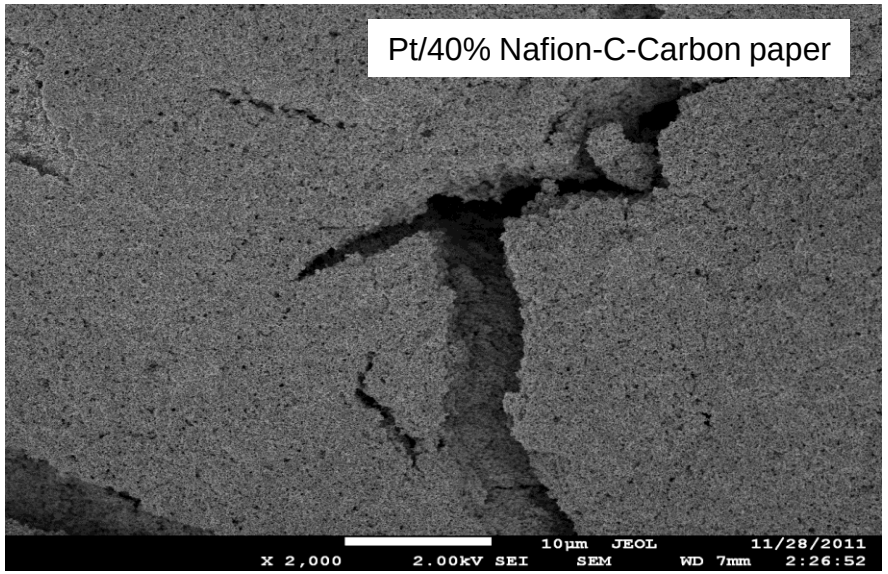


# Pt supported on FC gas diffusion layer: SEM micrographs and EDX profile



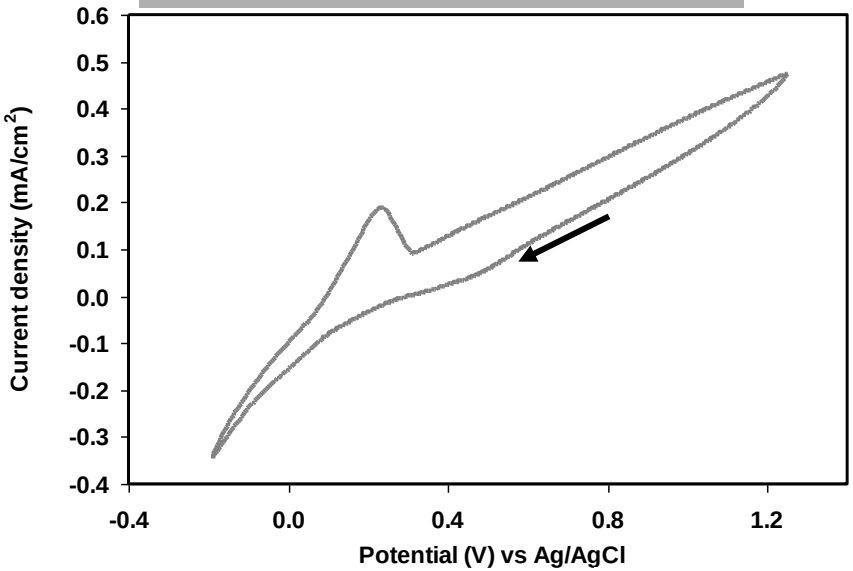



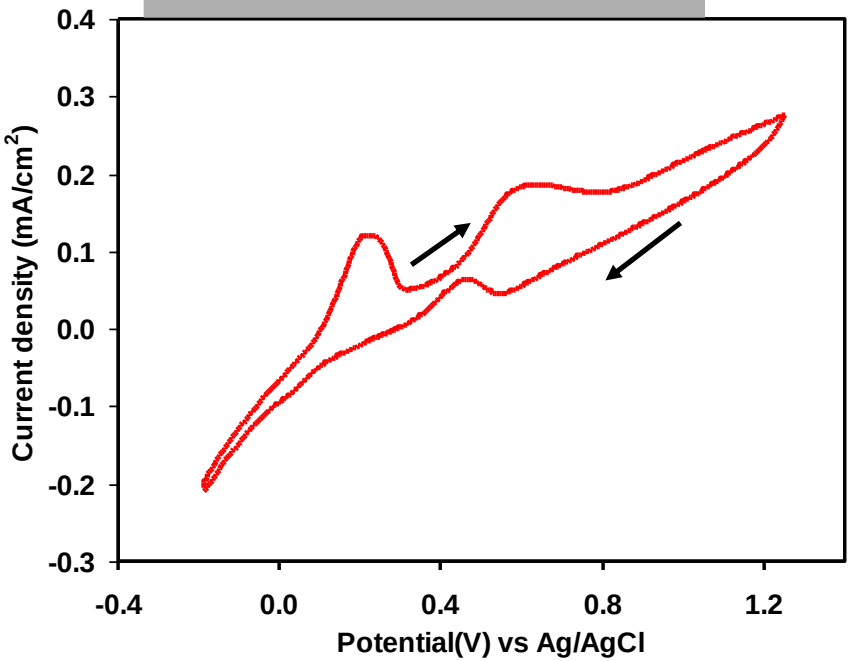
# Pt supported on Ti mesh: Electrochemical Evaluation

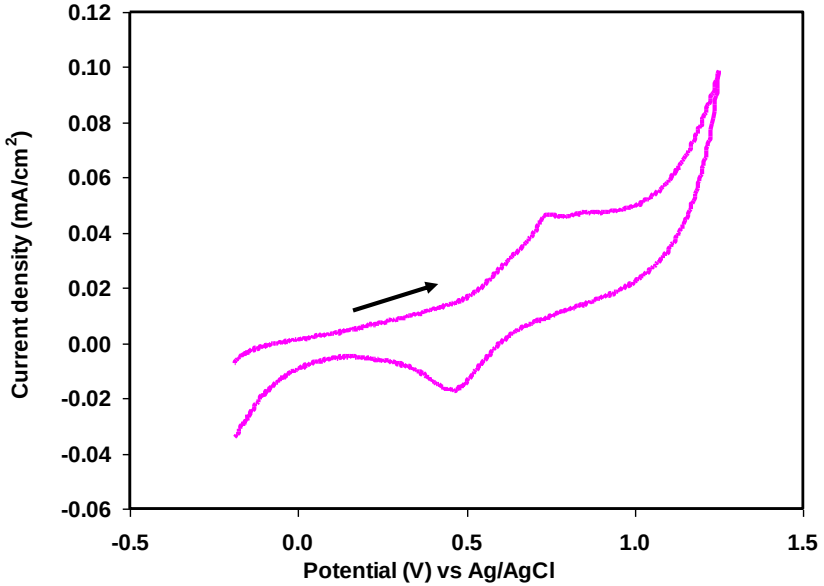
Cyclic voltammograms at 50 mV/s in

(i) 0.1 M $HClO_4$




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




(iii) 0.1 M $HClO_4$ + CO

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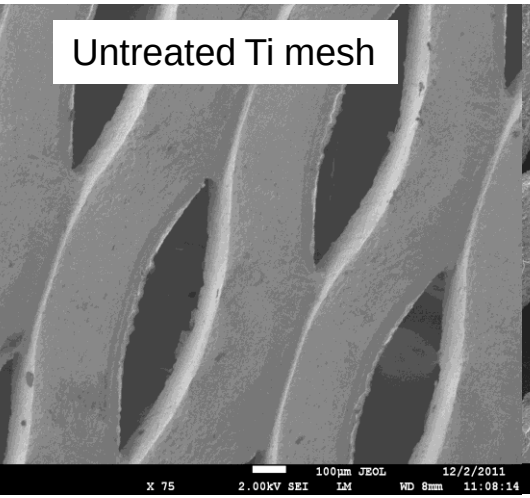
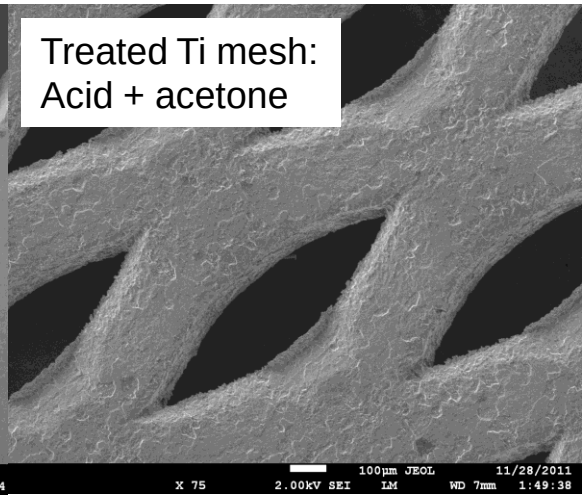
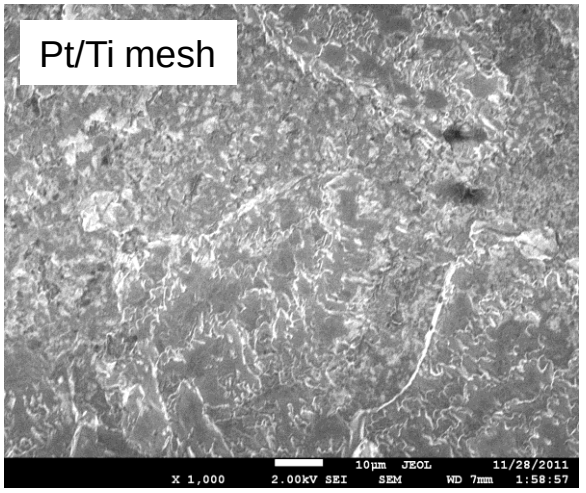
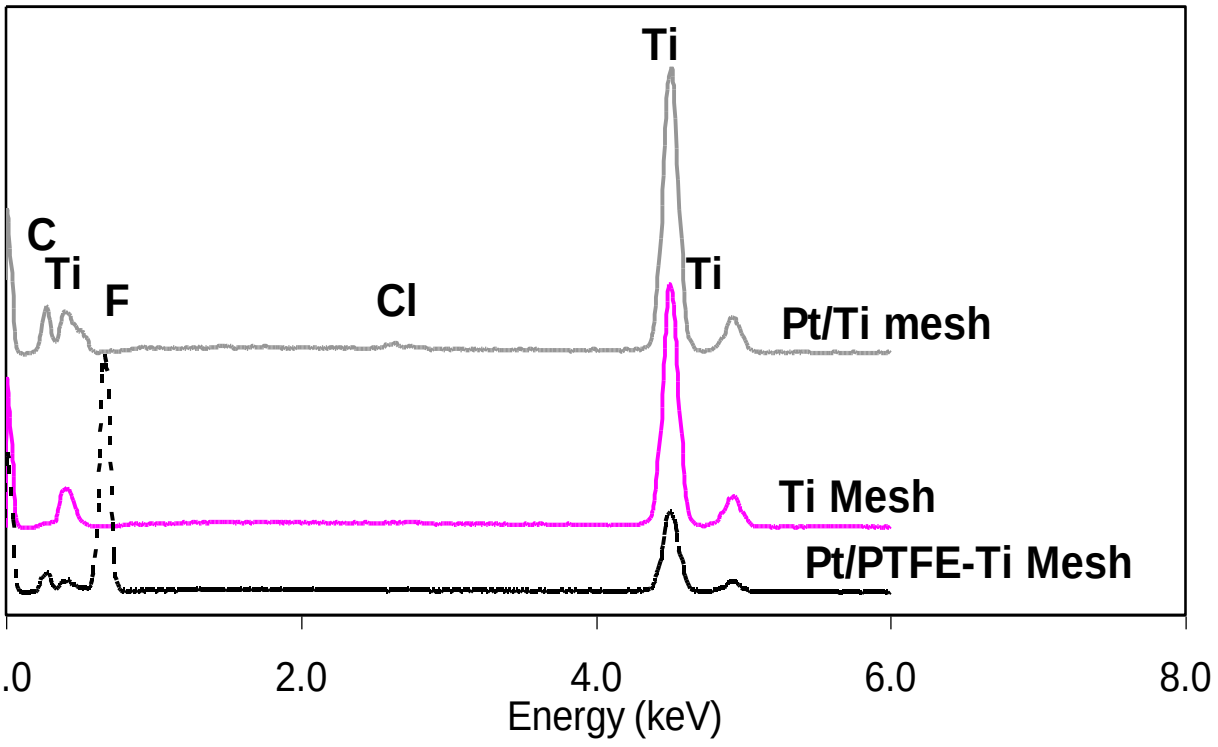
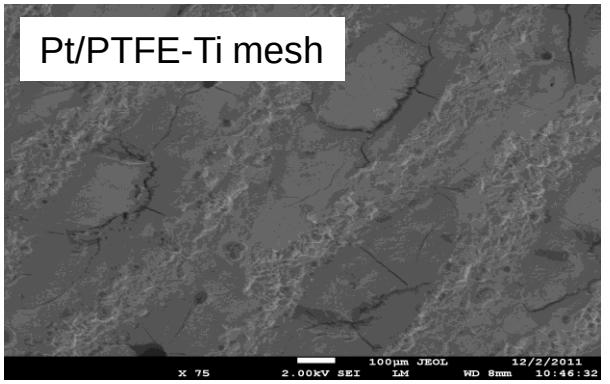
# Pt supported on Ti-mesh: SEM micrographs and EDX profile

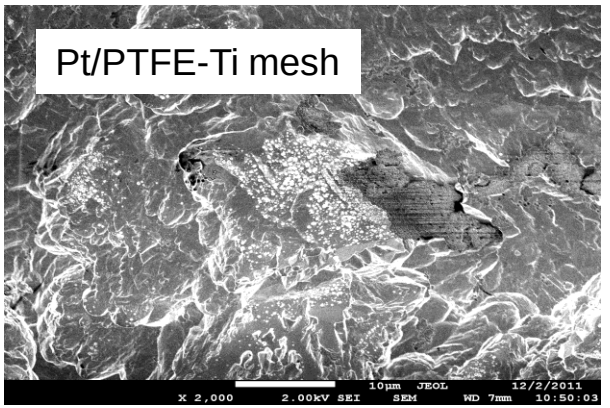


# Conclusions and Future work

- ECALD:
  - controlled growth of thin film deposits
  - atomic layer control is key to reducing the amount of PEMFC catalysts
- Substrates:
  - Ti mesh treatment: TiN, TiP, ITO
  - Other: Ni-based
- Fabricate MEA and test FC performance

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# Acknowledgements


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*Thank You*