Electrochemical Deposition and Characterization of Platinum on Carbon Paper and Ni Foam

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our future through science

Methanol Oxidation Mechanism

- $M + CH_3OH \rightarrow M\text{-}CH_3OH_{ads} \rightarrow M\text{-}CO_{ads} + 4H^+ + 4e^-$ (1)
- $M\text{-}CO_{ads} + H_2O \rightarrow M + CO_2 + 2H^+ + 2e^-$ (2)
- $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ (3)

BARBIR, F. (2005). Elsevier Academic Pres.

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Current Difficulties with Platinum

- Catalysts easily poisoned
- Cost too much

HAMMER, B., & NORSKOV, J. K. (2000). Academic Press Inc.

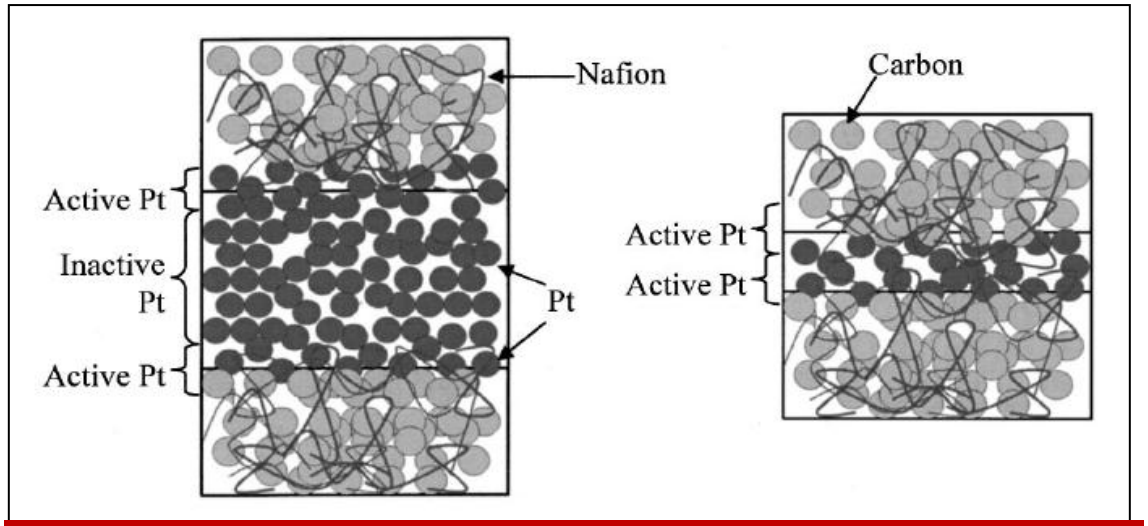
Current Difficulties with Platinum

- Catalysts easily poisoned
  - Binary or tertiary combinations
- Cost too much
  - Reducing Pt loading
  - Increasing surface area (Reactive area)

HAMMER, B., & NORSKOV, J. K. (2000). Academic Press Inc.

Pt Cost Consideration/Efficiency

- Reactions happen only on the surface



Demonstration of actual reactive area

HAUG, A.(2002). *Journal of The Electrochemical Society*, 149 , A284 -A287

Thin Film Deposition Techniques

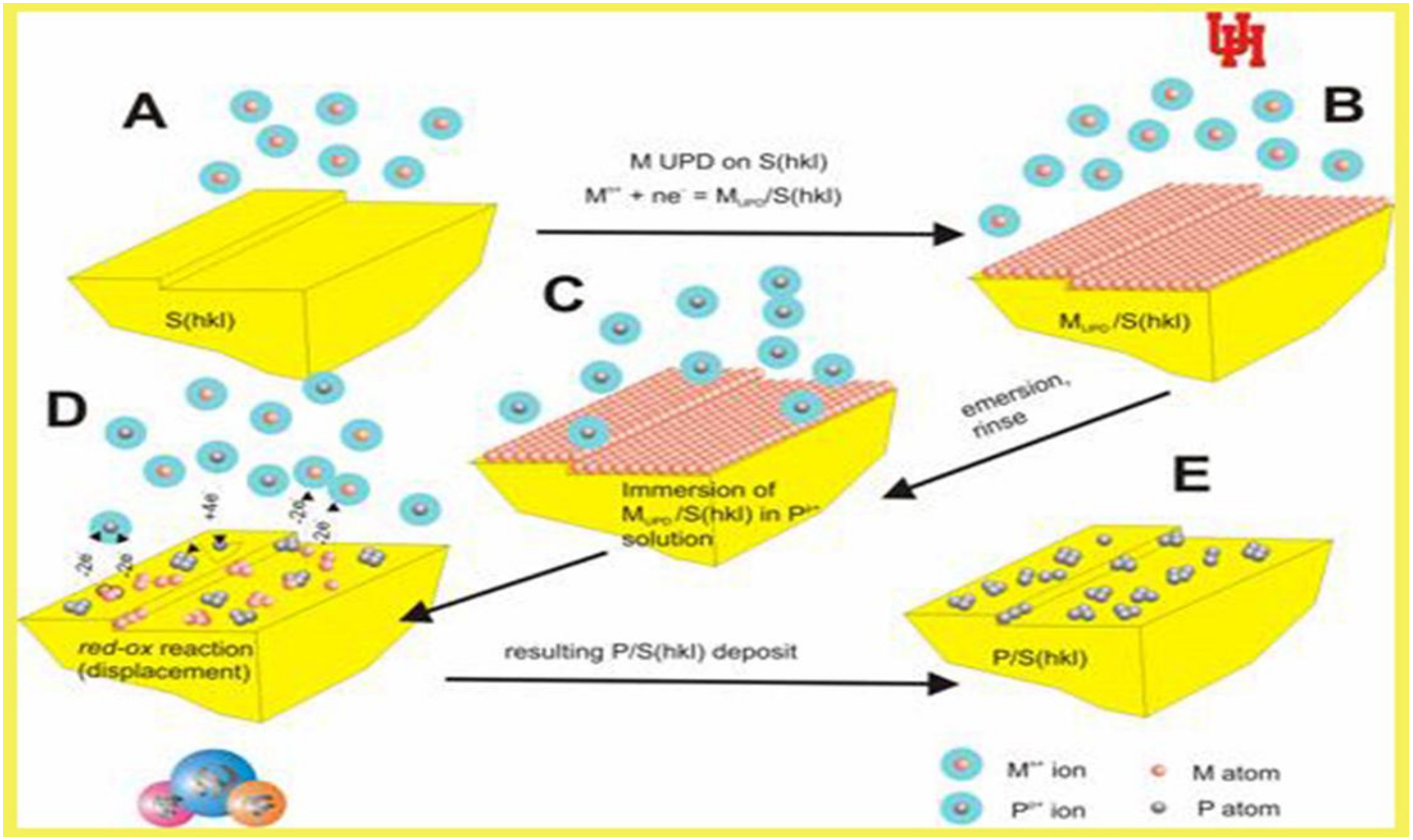
- Aerosol assisted deposition
- Physical or thermal deposition (e.g. Sputter deposition)
- Ion beam deposition
- Electrodeposition and
- Electrochemical atomic layer deposition (ECALD).

Reasons for ECALD Utilization

- Simplicity of operation
- Ease of control of the deposition
- Low cost of fabrication
- High Pt utilization

ADZIC, R. *et al.* (2007). *Topics in Catalysis, 46*, 249-262.

ECALD Process: Synthesis of Pt Electrocatalyst



Systematic diagram of Sequential electrodeposition coupled to Surface-limited Redox-replacement reactions

BRANKOVIC, S. *et al*. (2001). *Surface Science, 474*, L173.

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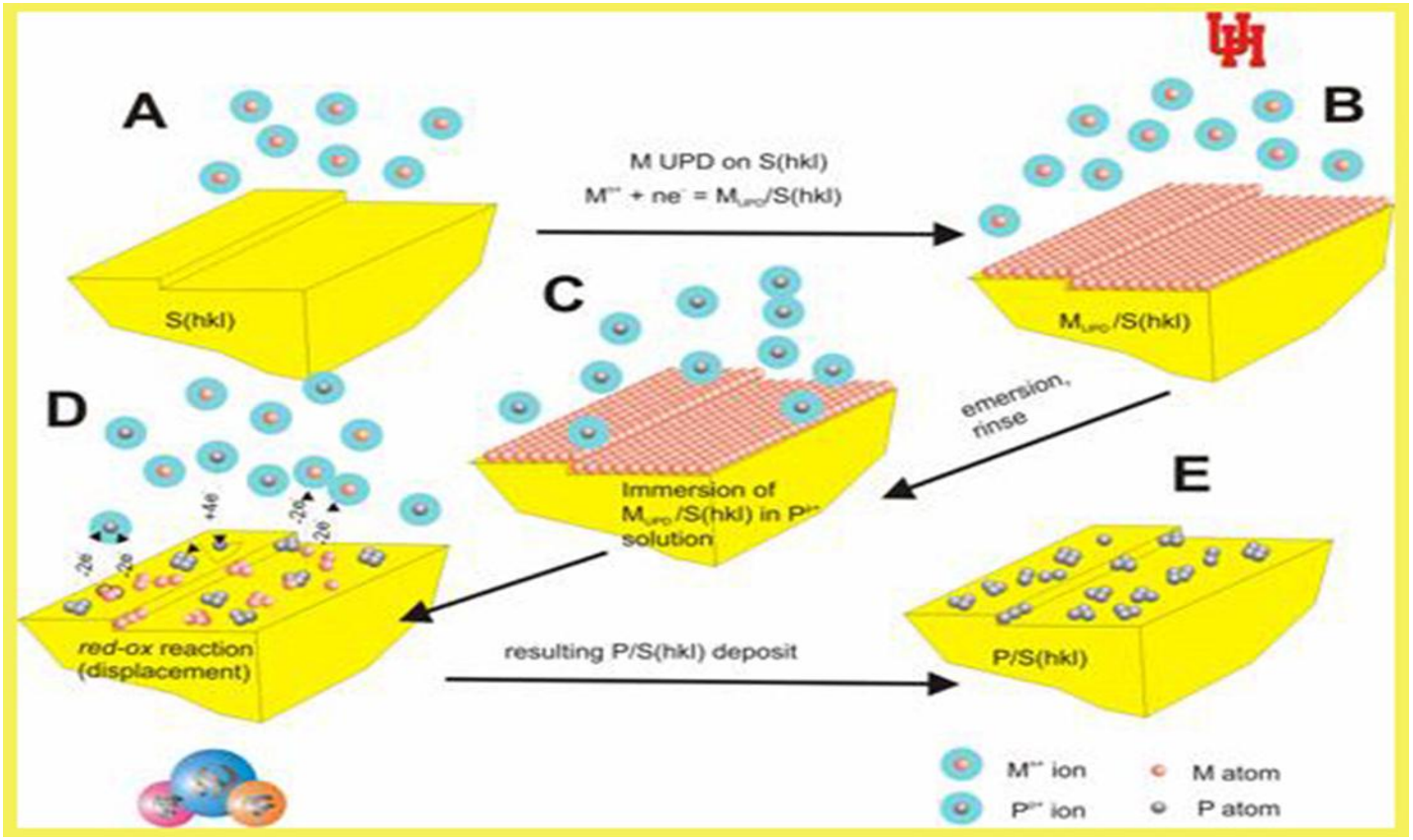


Systematic diagram of Sequential electrodeposition coupled to Surface-limited Redox-replacement reactions

A small OPD was used instead of UPD

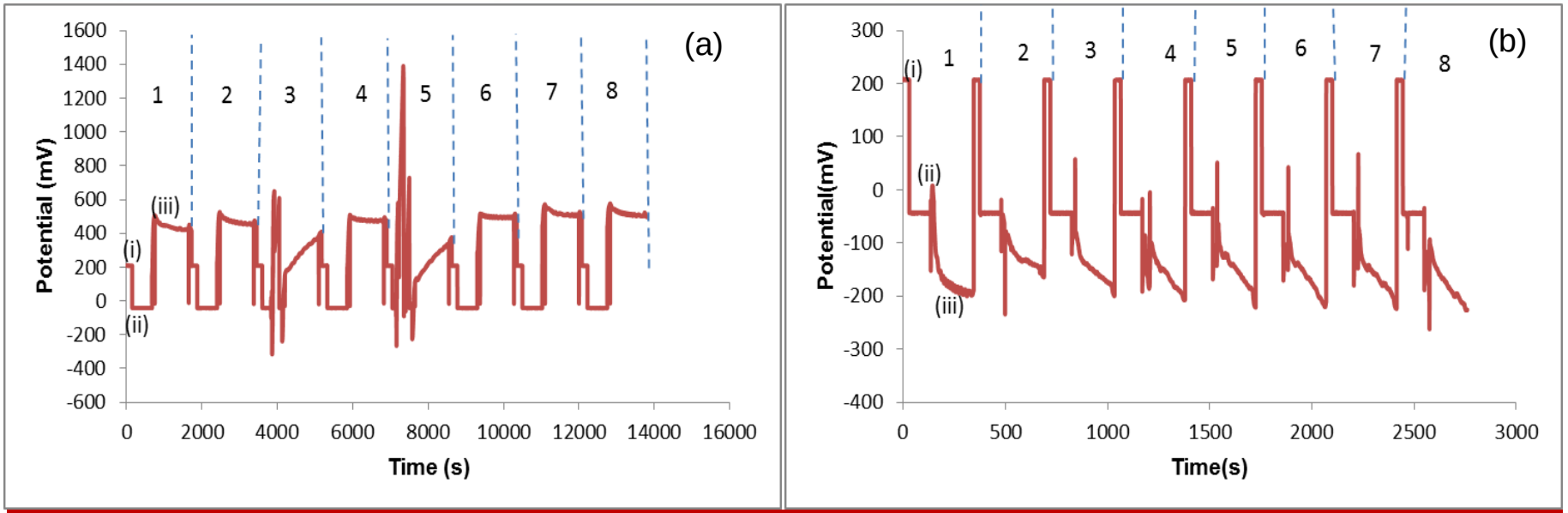
BRANKOVIC, S. *et al*. (2001). *Surface Science, 474*, L173.

Ni Foam and Carbon Paper

- High surface area
- Electrically and thermally conductive
- Chemically stable
- Low cost

HAMMER, B., & NORSKOV, J. K. (2000). Academic Press Inc.

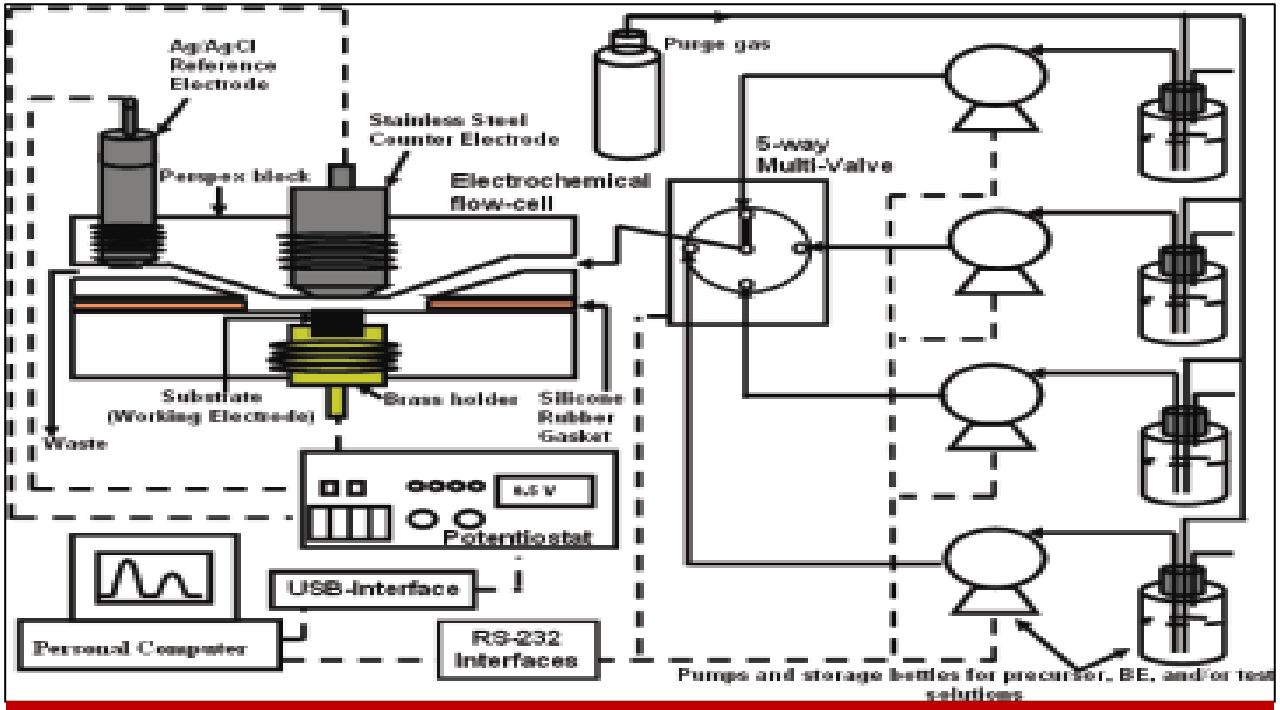
Time-Potential Curve



Time-potential curve recorded during Pt depositions on carbon paper (a) and Ni foam (b)

i. Rinse with BE at 0.2V
ii. OPD of Cu at -0.05V
iii. Galvanic displacement of Cu by Pt at OCP

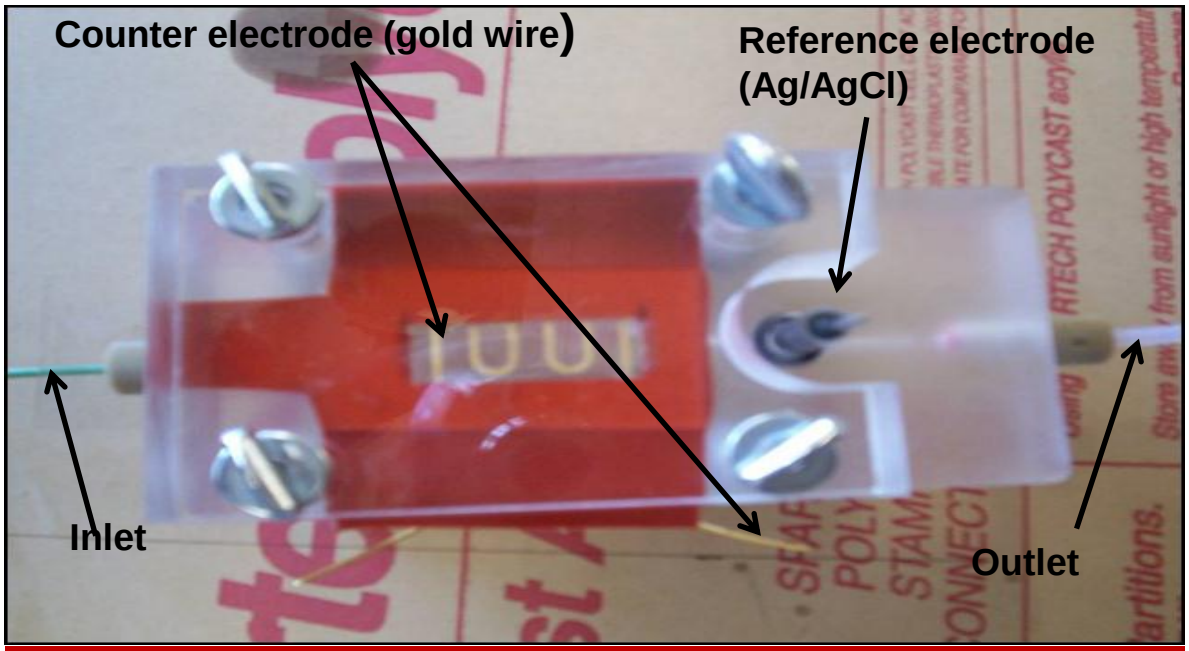
ECALD Instrument



Schematic diagram of the instrumental set up developed for automated electrodeposition using the flow cell

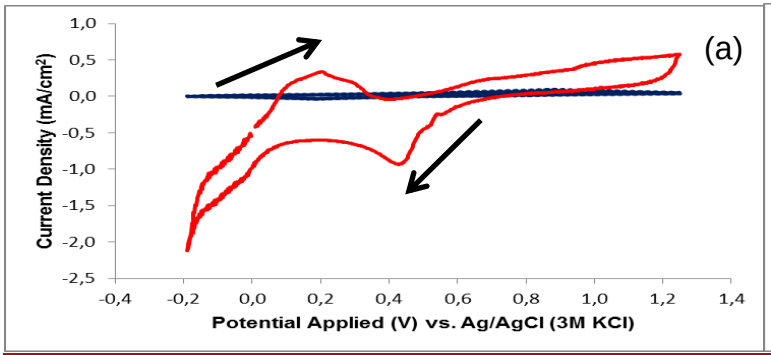
MKWIZU, T. S., MODIBEDI, M., & MATHE, M. (2011). *219th ECS Meeting*. Montreal, Canada: Journal of the Electrochemical Society

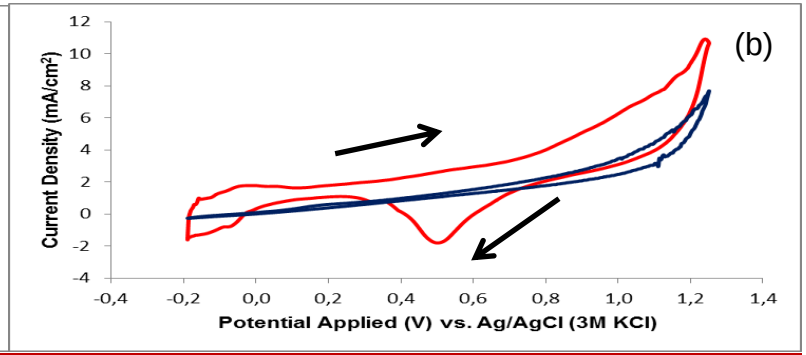
ECALD Flow-Cell



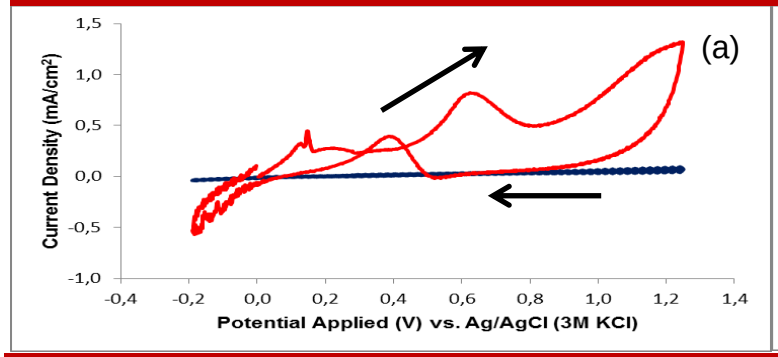
The photograph showing ECALD flow- cell

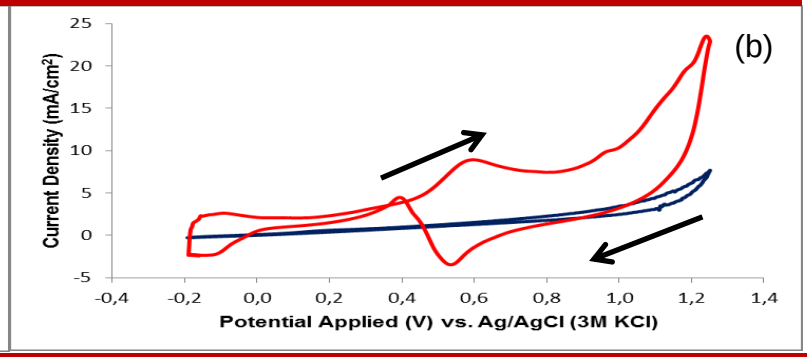
Cyclic Voltammograms





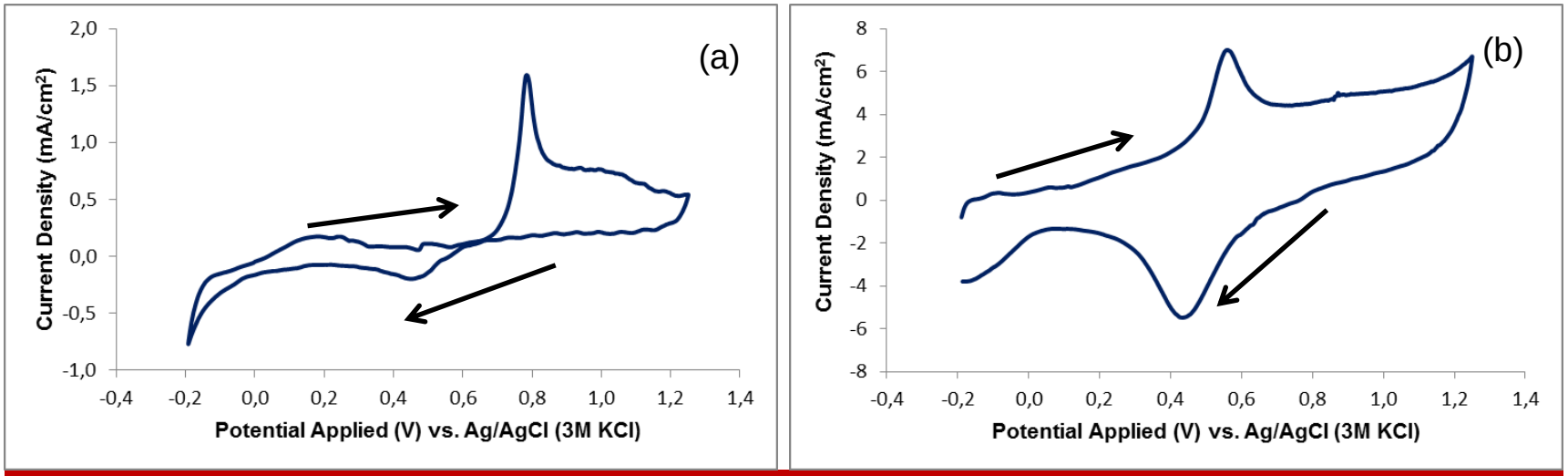
- Cyclic Voltammogram of Pt/Carbon paper (a) and Ni foam (b) at 50 mV/s in 0.1M $HClO_4$





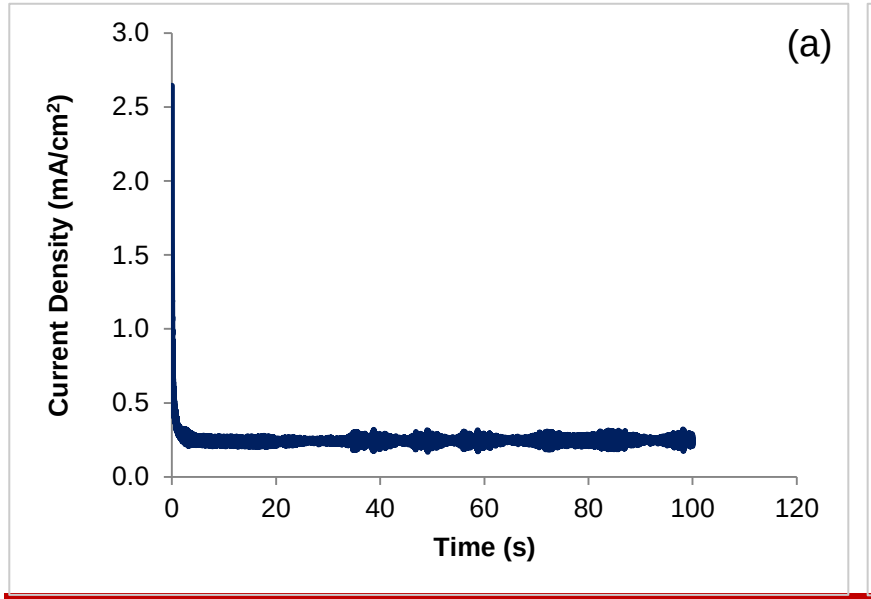
- Cyclic Voltammogram of Pt/Carbon paper (a) and Ni foam (b) at 50 mV/s in 0.1M $HClO_4$ and 0.1M MeOH

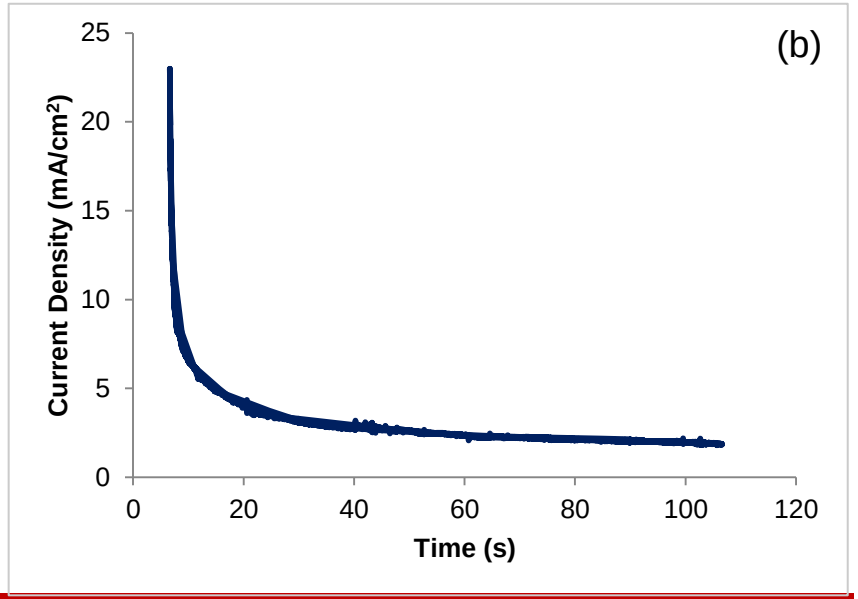
CO anodic Stripping



- Cyclic Voltammogram of Pt/Carbon paper(a) and Ni foam(b) at 50 mV/s in 0.1M $HClO_4$ and CO

Chronoamperometry



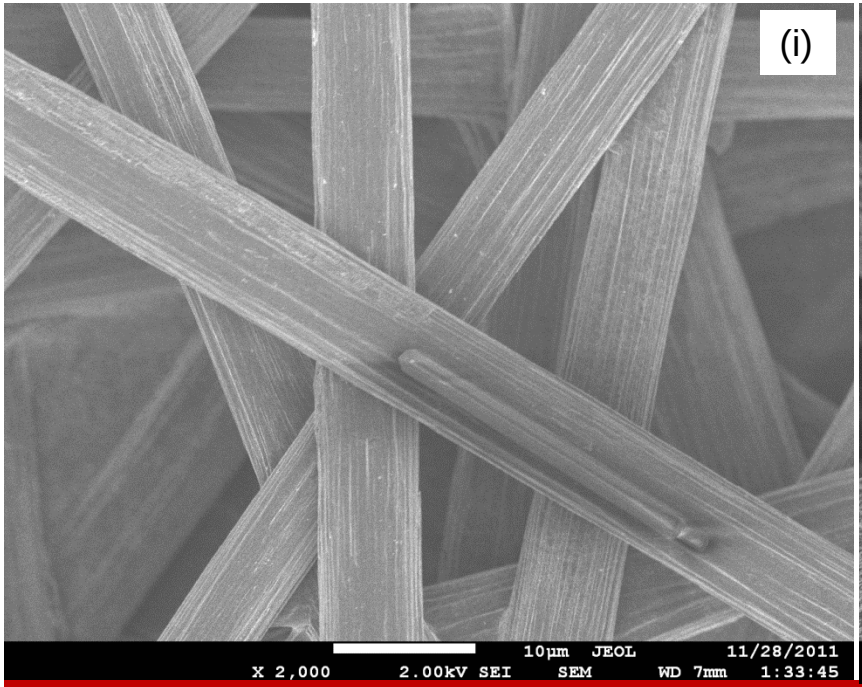


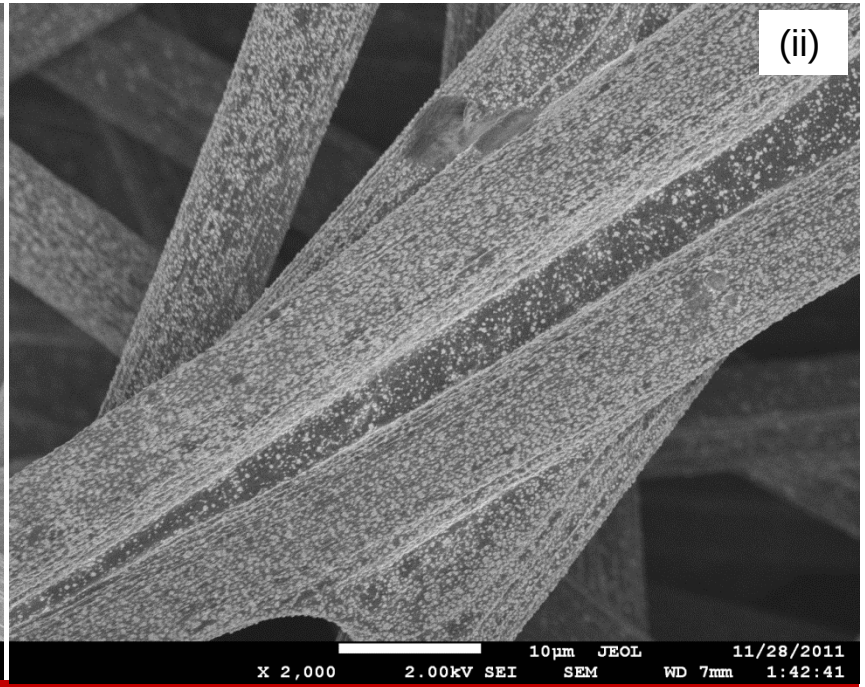
- Chronoampermetry measurements of Pt/Carbon paper(a) and Ni foam (b) at 50 mV/s in 0.1M $HClO_4$ and 0.1M MeOH

Summary of Pt Electrochemical Activities

Catalyst	Maximum Current Density (mA/cm^2)	Onset Potential (V) for MOR	I_f/I_r	Current Density (mA/cm^2) after 100 s	Onset Potential (V) for CO stripping	Real Surface Area (cm^2)
Pt/Carbon paper	0.85	0.40	4.30	0.30	0.66	479.08
Pt/Ni foam	5.94	0.37	2.81	1.90	0.37	1615.59

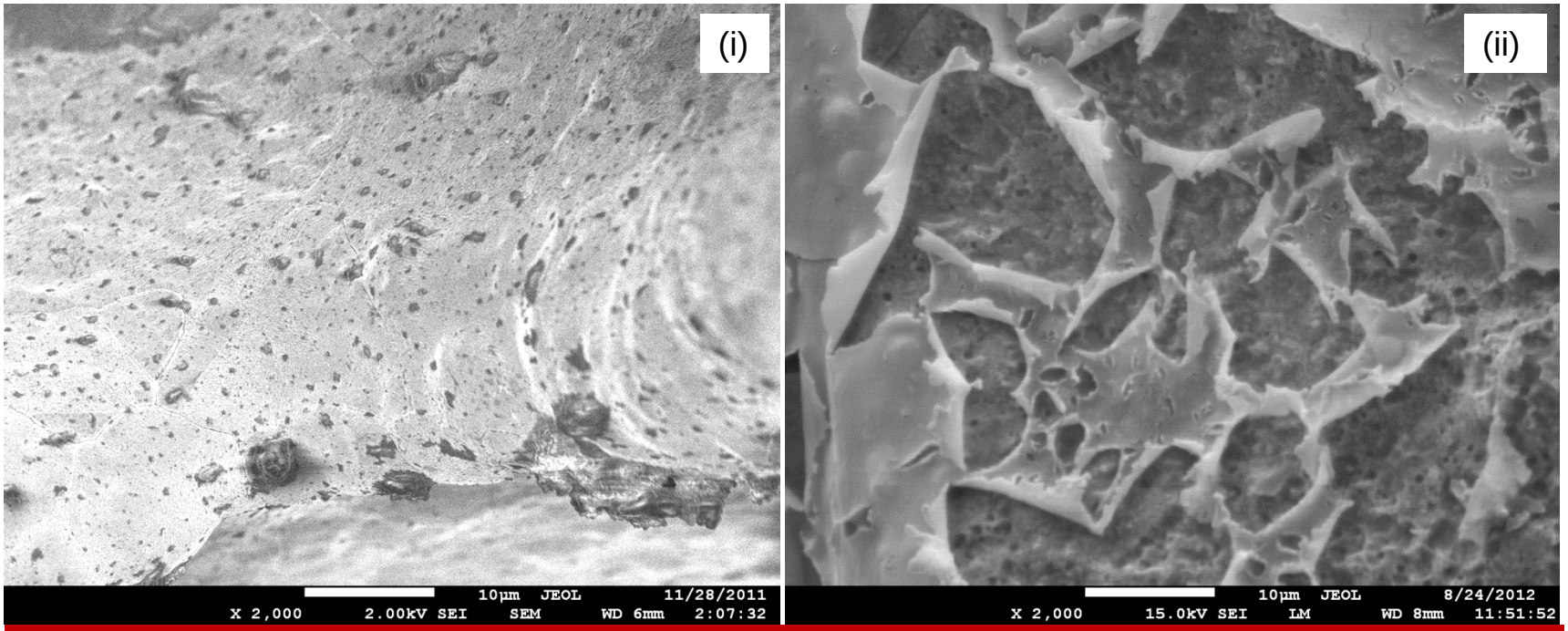
SEM Images for Carbon Paper





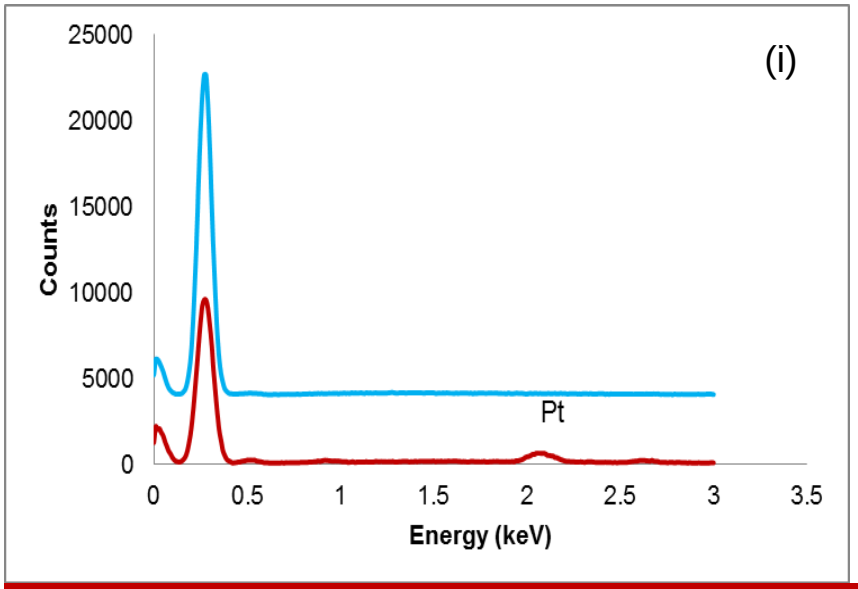
- SEM micrographs carbon paper before (i) and after (ii) deposition

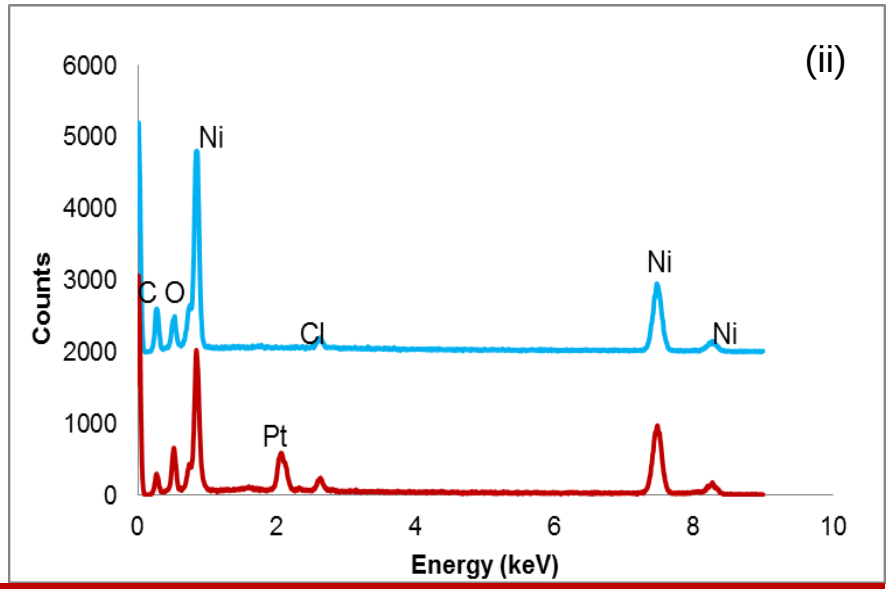
SEM Images for Ni Foam



- SEM micrographs of Ni foam before (i) and after (ii) deposition

EDX Profiles





- EDX profiles of carbon paper (i) and Ni foam (ii)

Conclusion and Future Work

- Preliminary results showed that the sequential electrodeposition of Pt on carbon paper and Ni foam were successful.
- Pt was detected with EDX and confirmed by the SEM images
- The sequential electrodeposited Pt on Ni foam showed better electrochemical activity towards hydrogen, methanol and CO adsorption.
- Fabricate and test MEA's performance in DMFC.

Acknowledgements

- Dr Mmalewane Modibedi (Co-Supervisor), *Energy Material Council for Scientific and Industrial Research (CSIR), Pretoria, South Africa*
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Thank You