Electro-deposition of Pd on Carbon paper and Ni foam via surface limited redox-replacement reaction for oxygen reduction reaction

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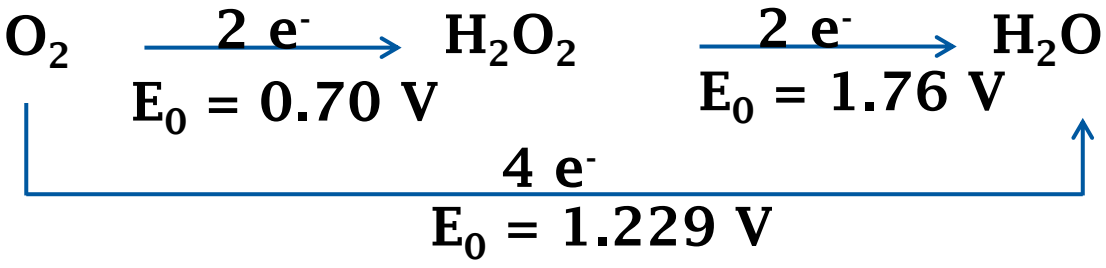
Outline of the presentation

- Introduction: Oxygen reduction reaction (ORR)
- Fuel cells: Proton exchange membrane (PEM) and Anion exchange membrane (AEM)
- Electrocatalysts: Preparation
- Electrocatalysts: Characterisation
- Electrocatalysts: Electrochemical evaluation
  - Acid electrolyte
  - Alkaline electrolyte
- Conclusions and Future Work

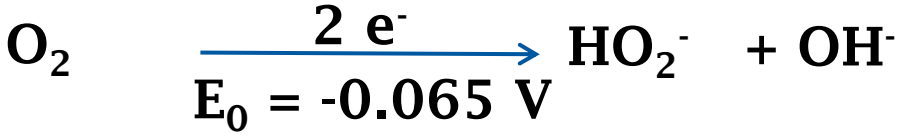
1. Oxygen reduction reaction (ORR)

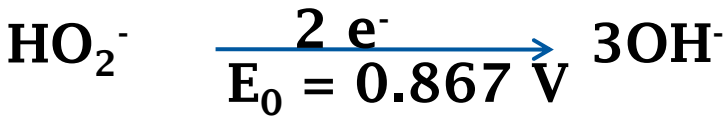
- ORR is most important reaction in life processes and energy converting systems: Fuel cells, Sensors

- ORR pathways in aqueous solutions:

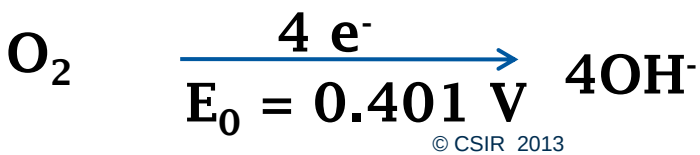


Acid aqueous electrolyte



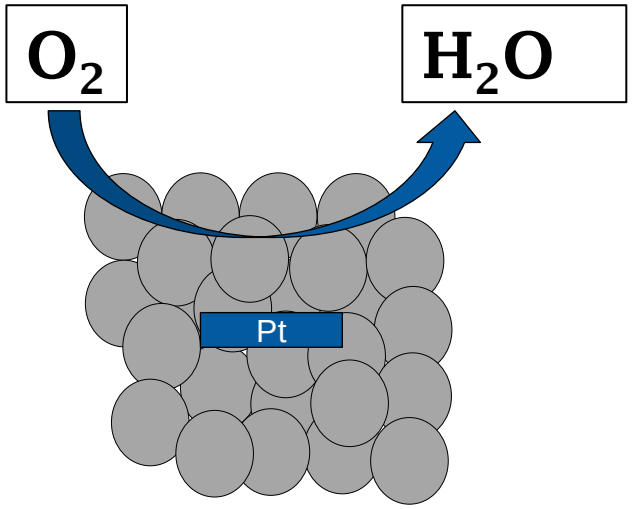


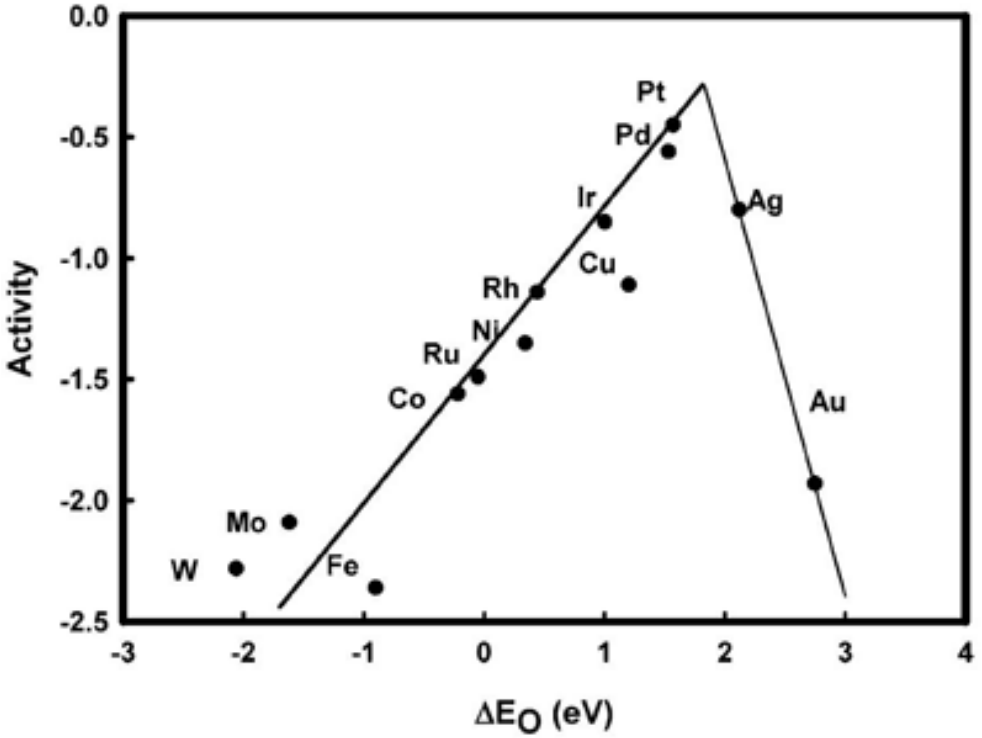
Alkaline aqueous electrolyte



1. ORR Catalysts

- ORR kinetics is very slow
  - Catalyst is essential
- Pt-based catalysts
- Alternative catalysts
  - Less expensive than Pt





Oxygen reduction activity on various transition metal electrodes as a function of the oxygen binding energy from DFT calculations.

J.K. Norskov et al. J. Phys. Chem. B 108 (2004) 17886

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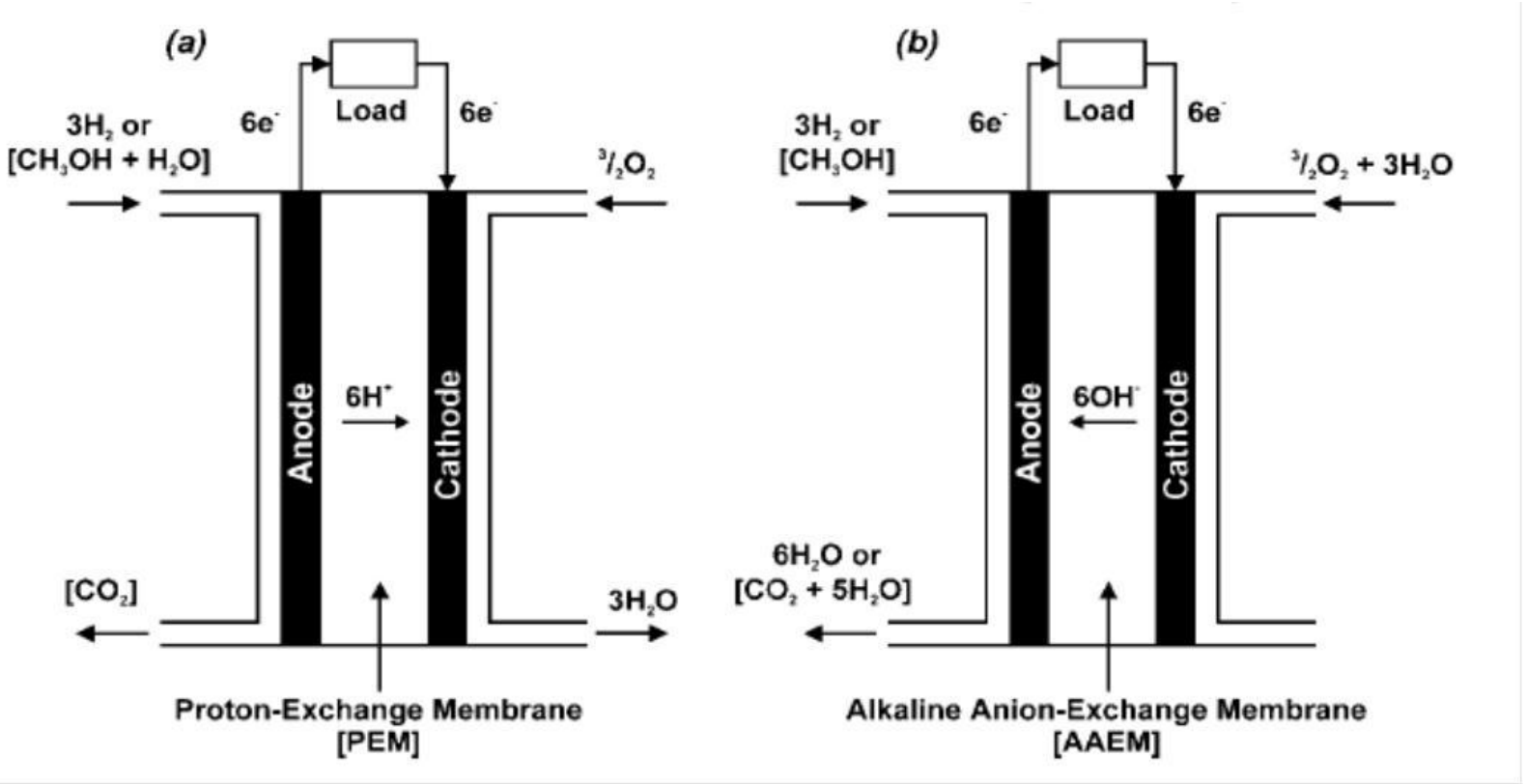
2. Fuel Cells

2.1 Low temperature PEMFC, DMFC, AEMFC



Why AAEM?

- Catalysts: use non-noble metals, faster kinetics of oxygen reduction and alcohol oxidation
- Membrane: reduced or no alcohol crossover

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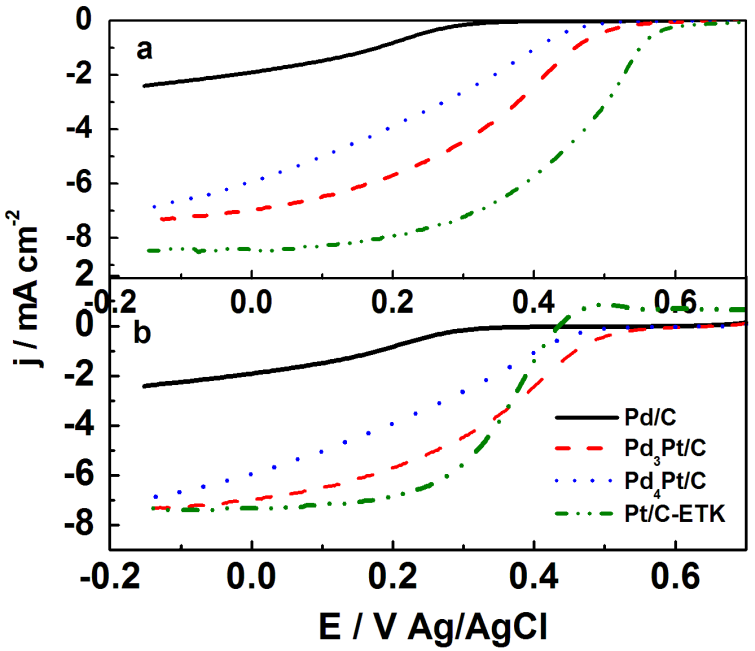
3. Electrocatalysts

3.1 Preparation methods

- Sonochemistry
  - Pt, Pd_3Pt on Carbon black



- Microwave-assisted alcohol reduction
  - Ru on N-doped CNTs

Electrode	Onset potential V	No of electron transferred at (1500 rpm, -0.30V)	Limiting current density (mA/cm^2)
N-CNTs	-0.166	2.4	-2.95
2Ru/N-CNTs	-0.158	3.9	-4.76
5Ru/N-CNTs	-0.153	3.7	-4.54
10Ru/N-CNTs	-0.148	3.2	-3.66

Mabena, Modibedi et al., Fuel Cells 12(5) (2012) 862

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3. Electrocatalysts

3.1.1 Electrochemical atomic layer technique (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

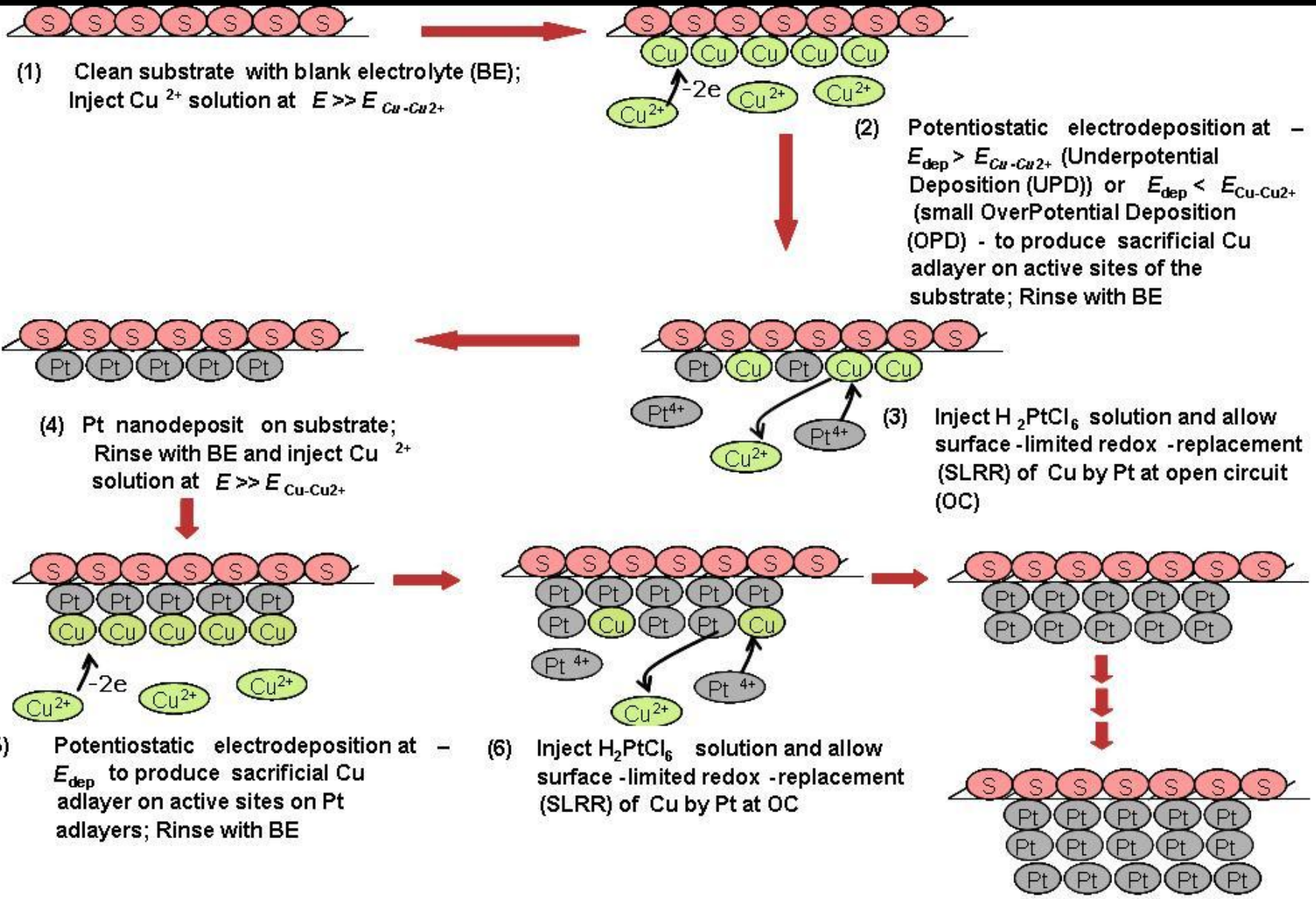
Advantages:

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

Offers atomic layer control- fundamental for controlled growth processes

Stickney, J.L., et al., Electrodeposition of Compound Semiconductors by Electrochemical Atomic Layer Epitaxy (EC-ALE), in Encyclopedia of Electrochemistry, A.J. Bard and M. Stratman, Editors. 2002, Wiley-VCH: Weinheim: p. 513-560
T.S.Mkwizu, M.K. Mathe, and I. Cukrowski, Langmuir, Vol. 26, 570 - 580 (2010)

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

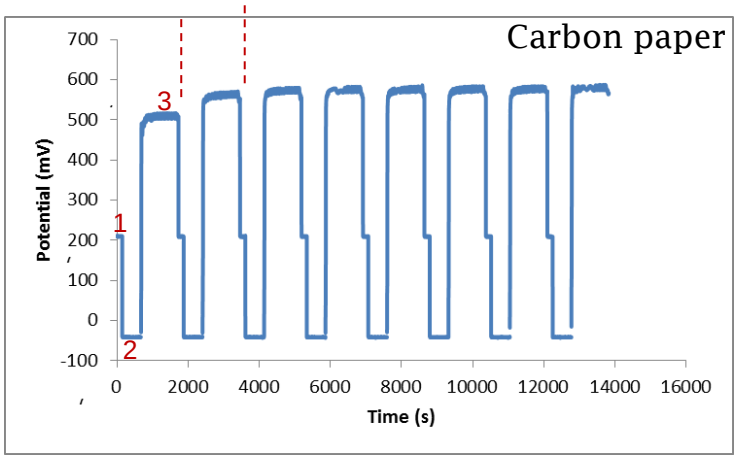
3.1.1 ECALD cont'd:

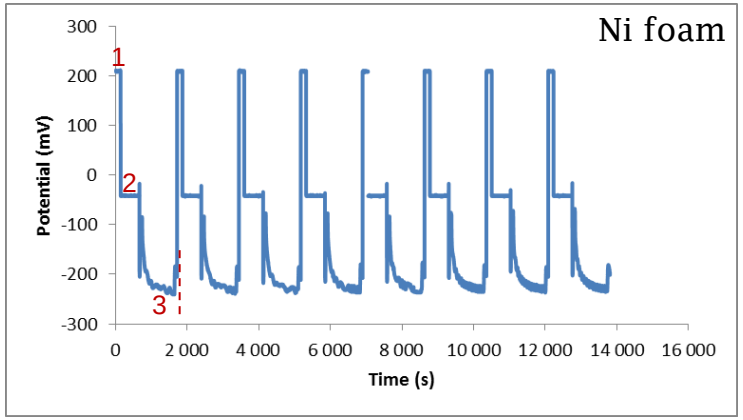
Noble-Metal: Pd

Substrates: Carbon paper, Ni foam

Repeat cycles 1X, 4X, 8X: 8X, Small OPD

- **Cu(s) deposition occurs through kinetically controlled 3D nucleation**





1. Rinse cell with BE at 0.2V, rinse with Cu^{2+} solution
2. Cu deposition at -0.05V, rinse with BE at -0.05V
3. Rinse with Pd^{2+} solution at OCP, SLRR at OCP

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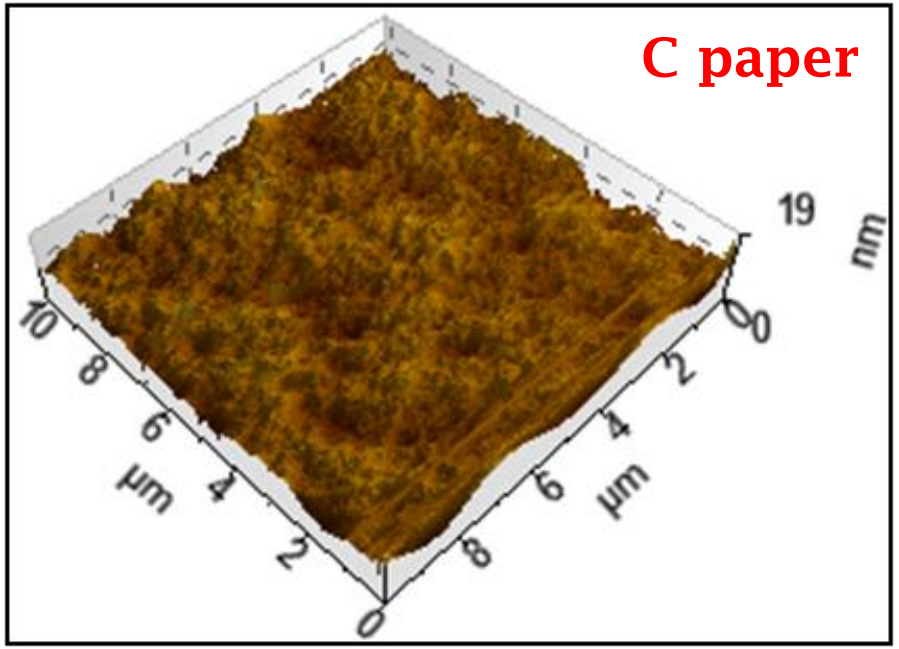
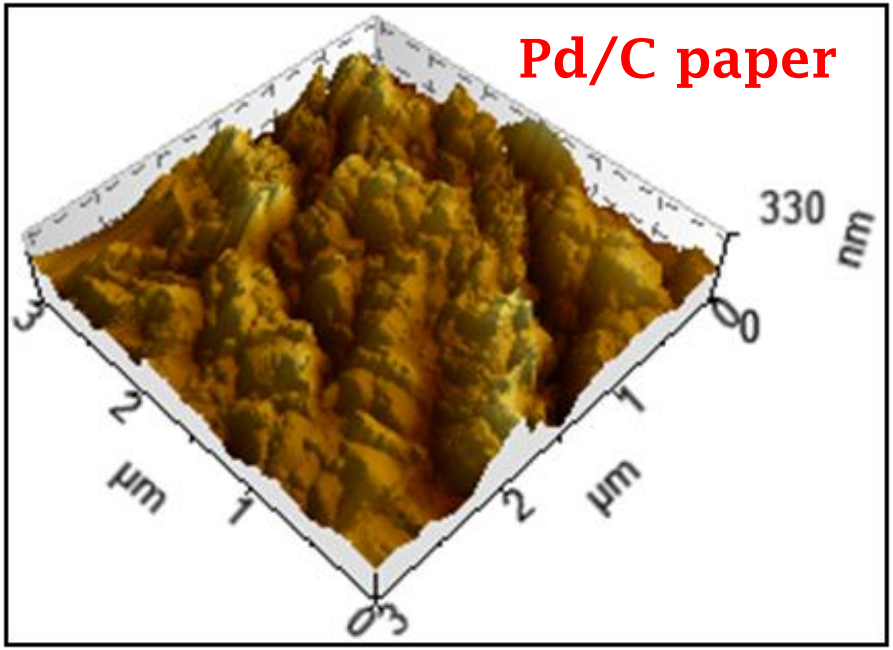
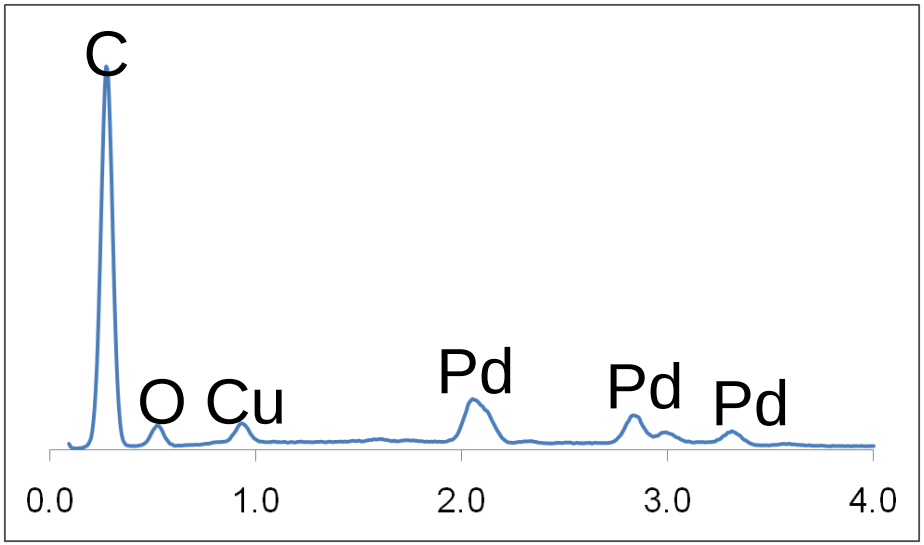
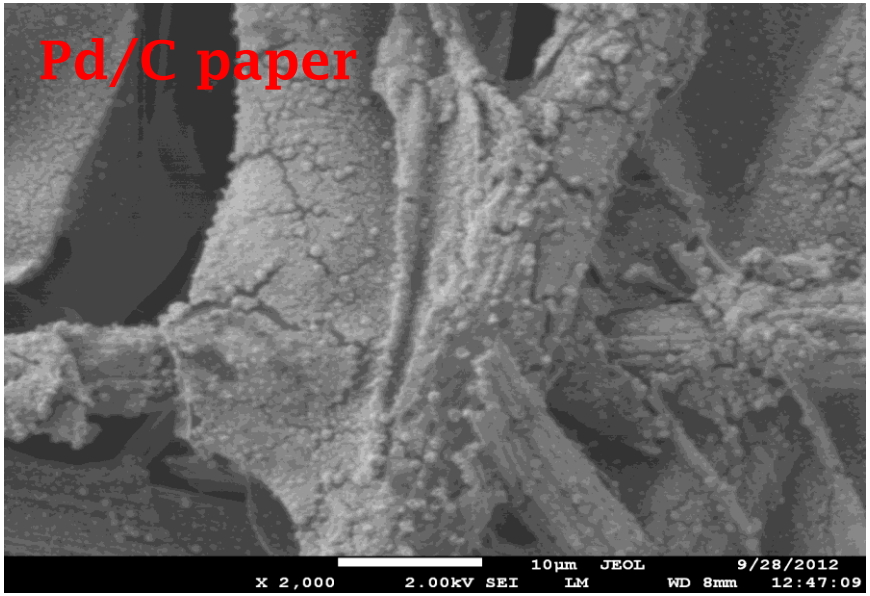
Modibedi et al., ECS Trans. 50, 2013

Pd/carbon paper: SEM, AFM micrographs and EDX profile

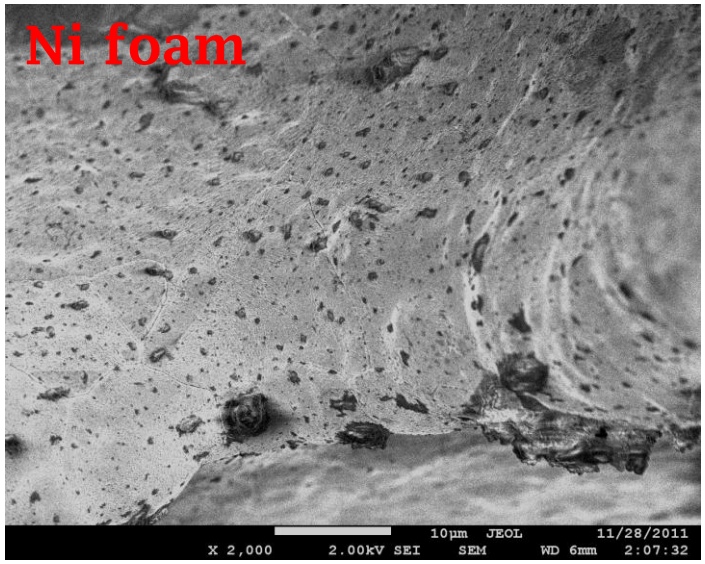


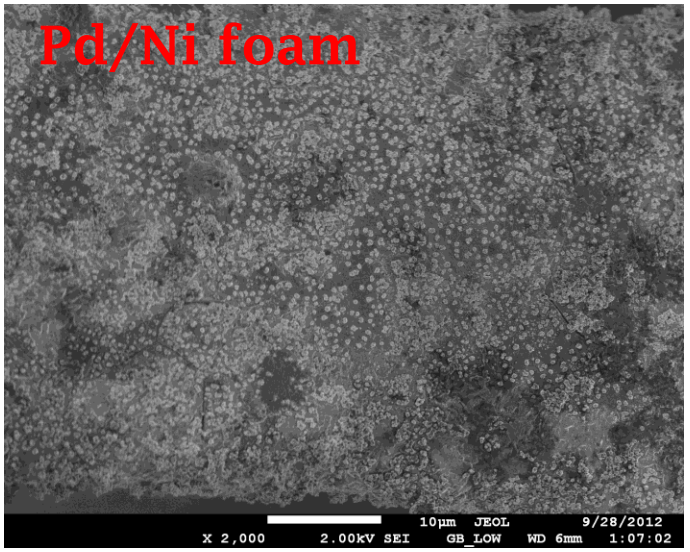


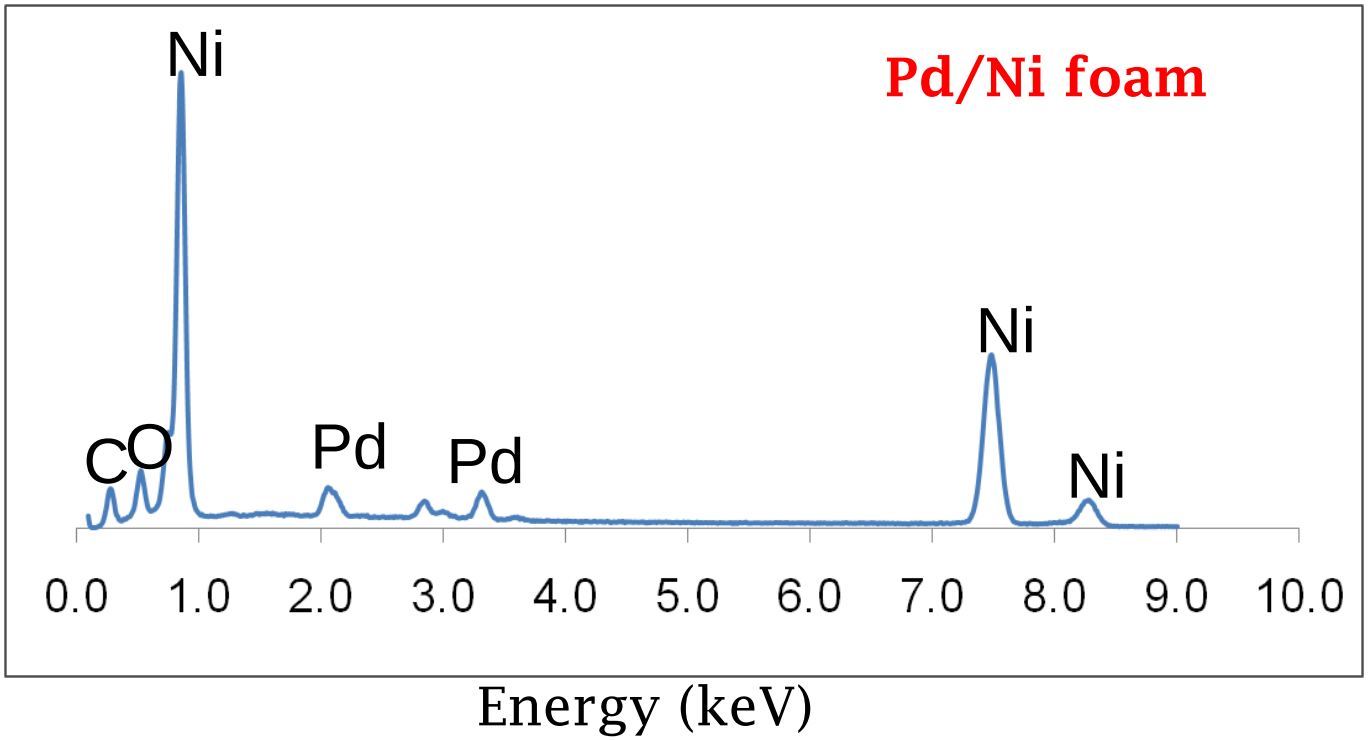




Pd/Ni foam: SEM micrographs and EDX profile







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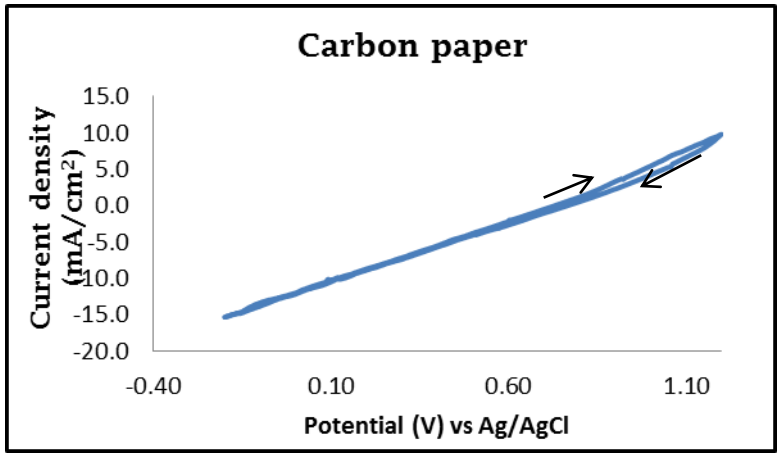
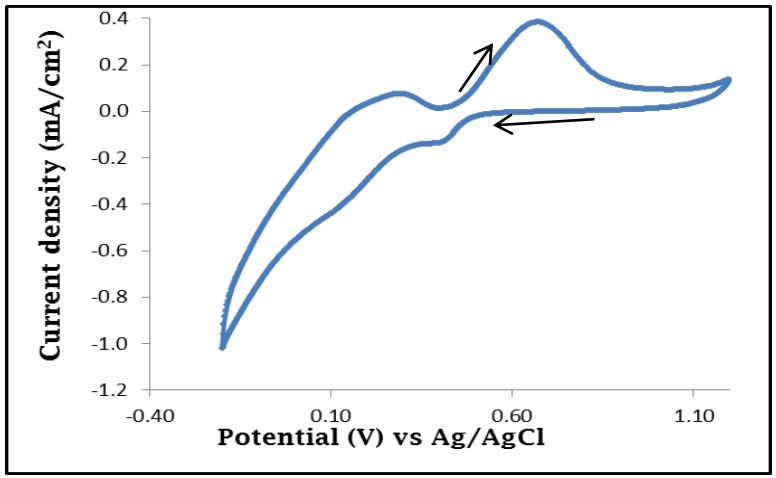
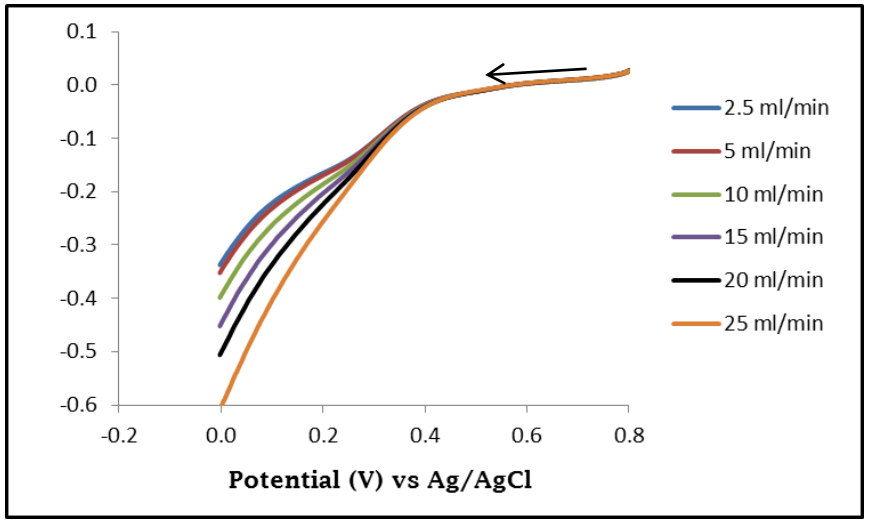
Pd/Carbon paper: Electrochemical Evaluation

(i) CV in 0.1 M $HClO_4$ + N_2 at 50 mV/s





(ii) LSV in 0.1 M $HClO_4$ + O_2 at 10 mV/s



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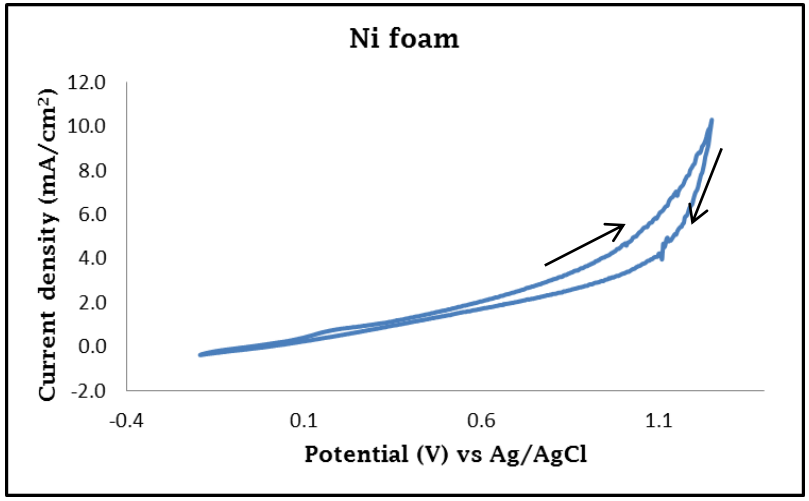
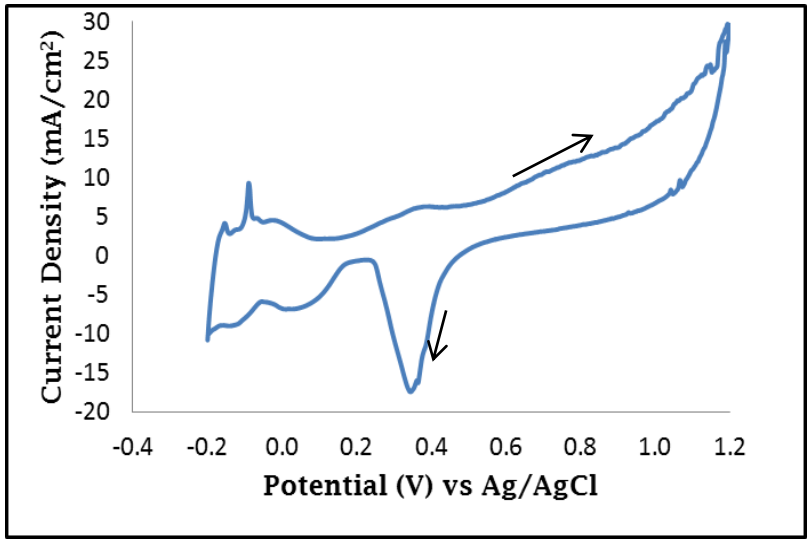
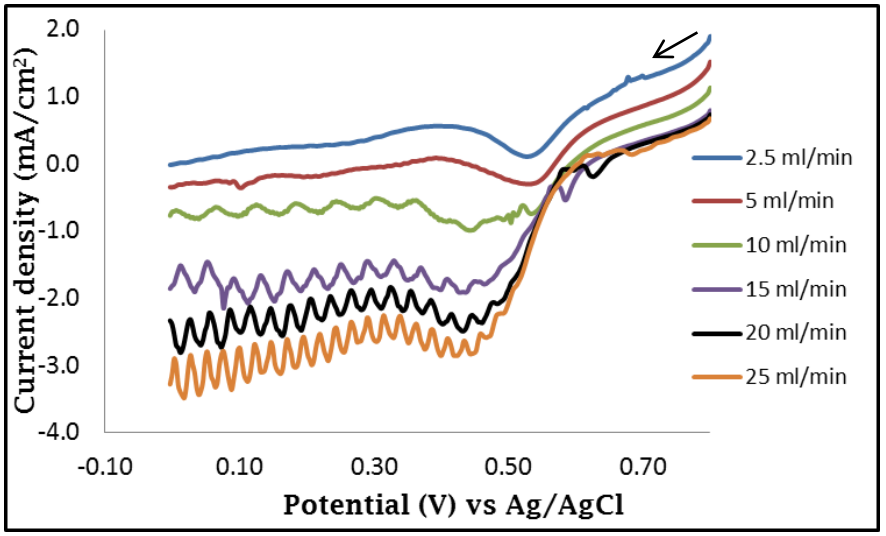
Pd/Ni foam: Electrochemical Evaluation

(i) CV in 0.1 M $HClO_4$ + N_2 at 100 mV/s





(ii) LSV in 0.1 M $HClO_4$ + O_2 at 10 mV/s



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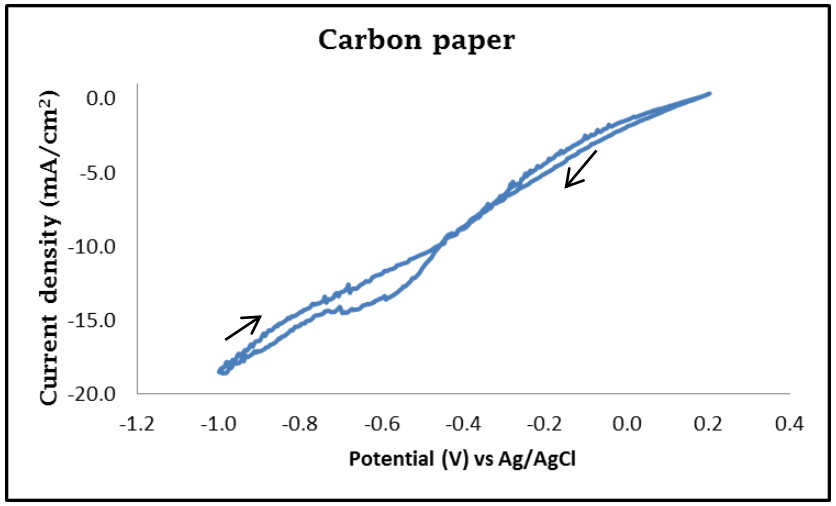
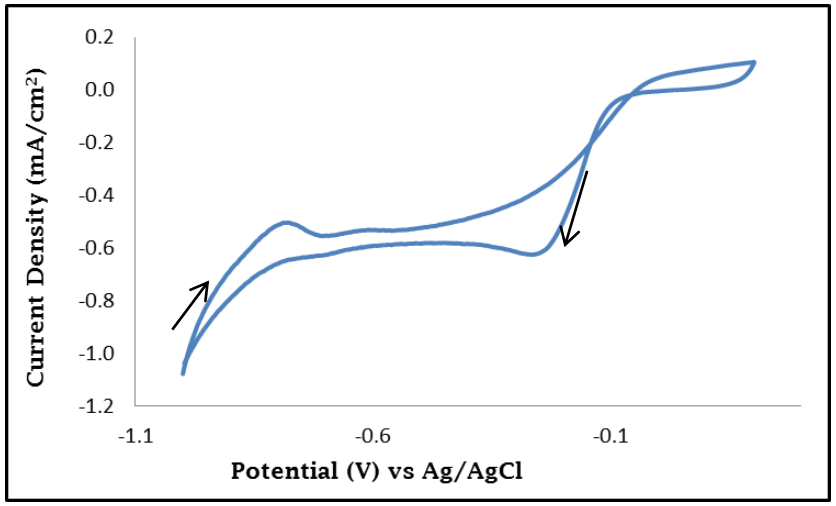
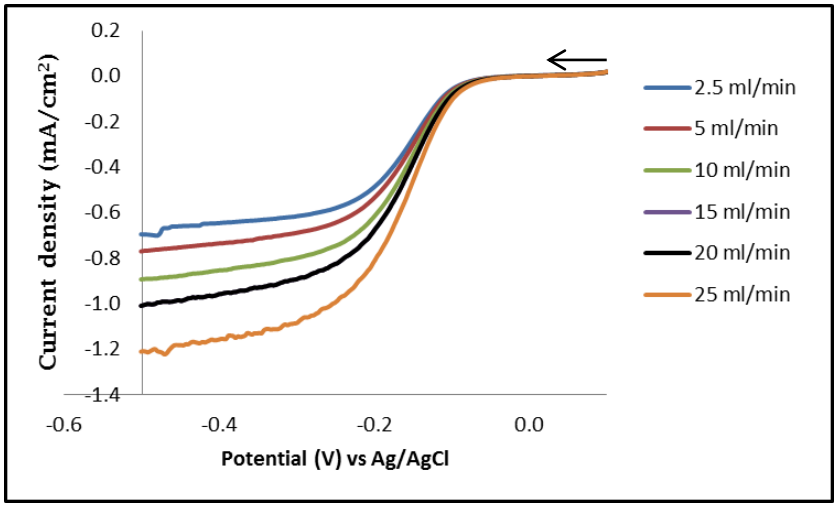
Pd/Carbon paper: Electrochemical Evaluation

(i) CV in 0.1 M KOH + N2 at 50mV/s





(ii) LSV in 0.1 M KOH + O_2 at 10mV/s



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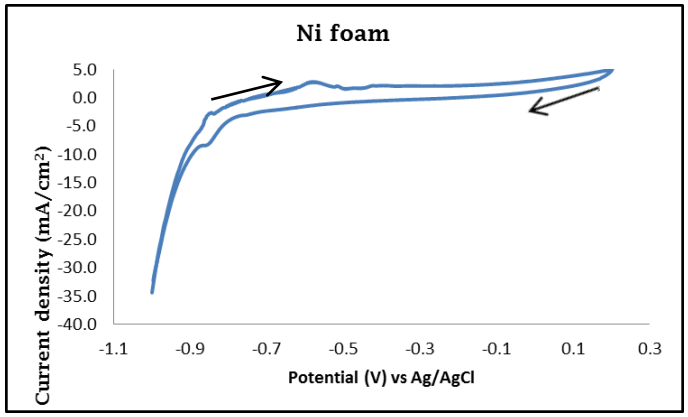
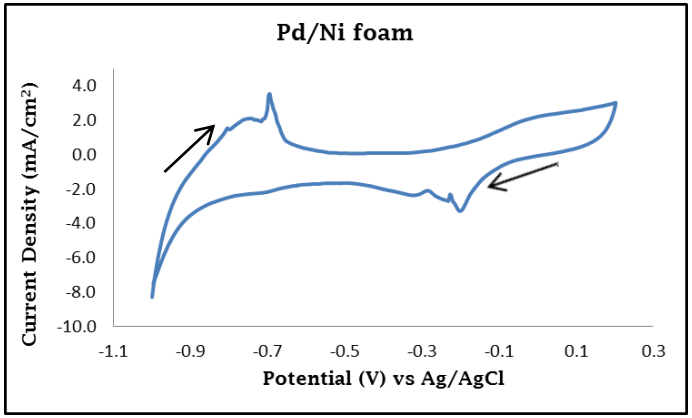
Pd/Ni foam: Electrochemical Evaluation

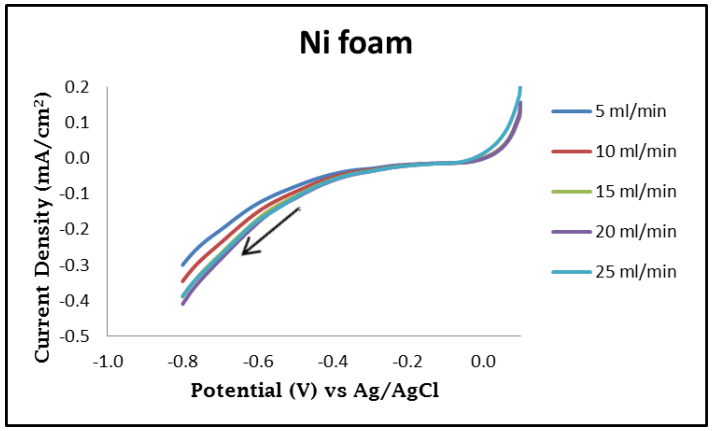
(i) CV in 0.1 M KOH + N_2 at 100 mV/s

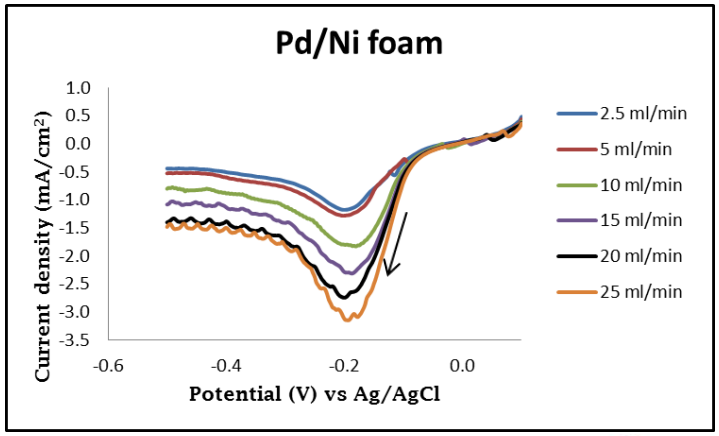


(i) CV in 0.1 M KOH + N_2 at 100 mV/s



(ii) LSV in 0.1 M KOH + O_2 at 10 mV/s





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Electrochemical evaluation: summary

at 15 ml/min

Electro-Catalyst	Onset potential (V) vs Ag/AgCl	Limiting current density (mA/cm^2)
Pd/C paper in acid	0.407	0.4492
Pd/Ni foam in acid	0.606	1.8862
Ni foam in alkaline	-0.508	0.400
Pd/C paper in alkaline	-0.073	0.880
Pd/Ni foam in alkaline	-0.052	2.2985

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Conclusions

- Pd nanoclusters were successfully deposited using SLRR
- Pd distribution on substrates was not uniform
- Pd/Ni foam improved performance vs. carbon paper
  - More positive onset potential
  - High current density

Future Work

- Incorporate complexing agents (Chloride) for uniform distribution of Pd on substrates: slow the exchange rate
- Synthesize binary electrocatalysts: DMFC
- MEA fabrication and FC testing under active conditions
- Investigate other “sacrificial metals” that will allow UPD deposition on C-and Ni- based substrates

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