Electrodeposition of Pd based binary catalysts on Carbon paper 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- Direct alcohol fuel cells (DAFC)
- Electrocatalysts:
  - Preparation
  - Characterisation
  - Electrochemical evaluation
- Conclusions
- Future Work

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1. Oxygen reduction reaction (ORR)

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

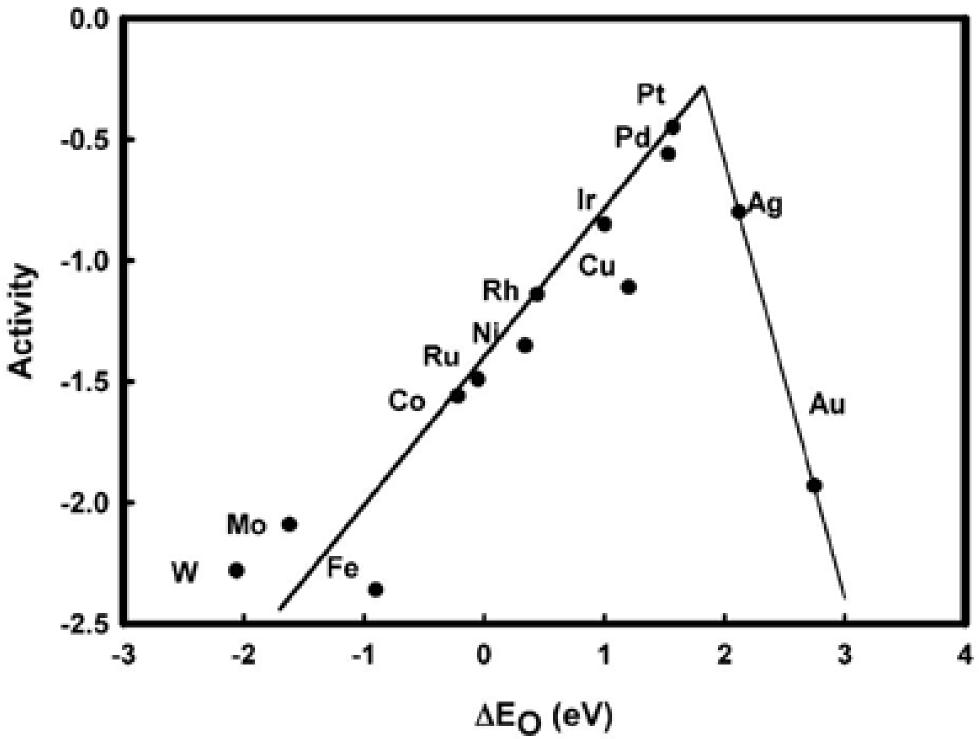
- ORR pathways in aqueous acidic solution:

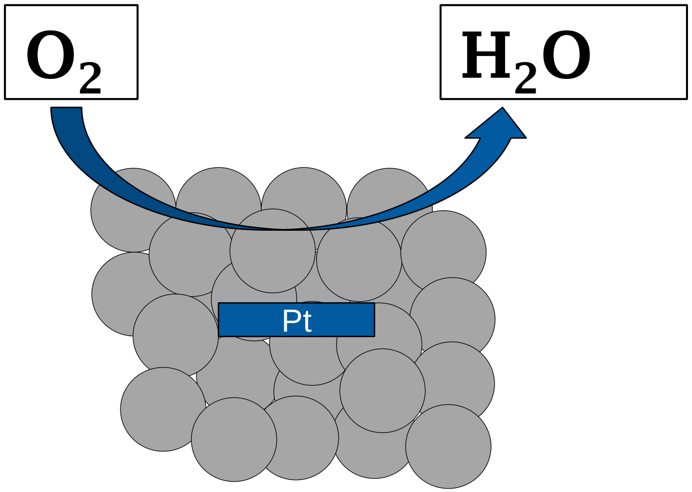
$$O_2 \xrightarrow[E_0 = 0.70\ V]{2\ e^-} H_2O_2 \xrightarrow[E_0 = 1.76\ V]{2\ e^-} H_2O$$

$$O_2 \xrightarrow[E_0 = 1.229\ V]{4\ e^-} H_2O$$

Preferred pathway for FC application: 4e-

1. ORR Catalysts





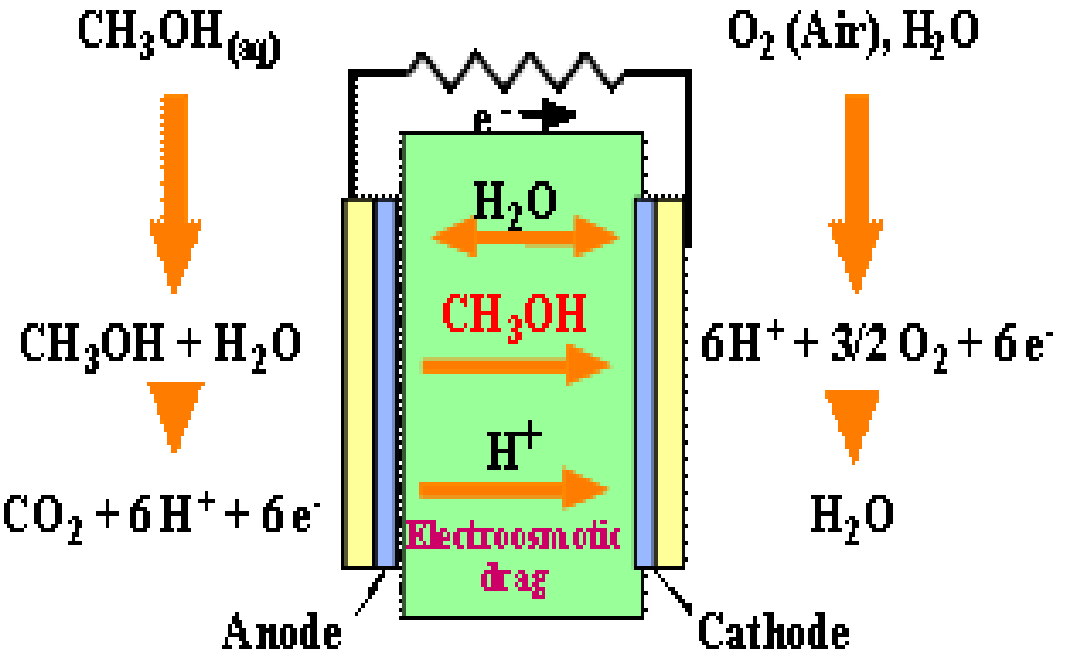
Oxygen reduction activity on various transition metal electrodes as a function of the oxygen binding energy from DFT calculations.

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

2. Direct Alcohol Fuel Cells

CHALLENGES:

- Sluggish reaction: better performing ORR catalyst
- High cost of catalyst: reduce amount of Pt, alternative catalysts
- Alcohol crossover: alcohol tolerant catalyst



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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

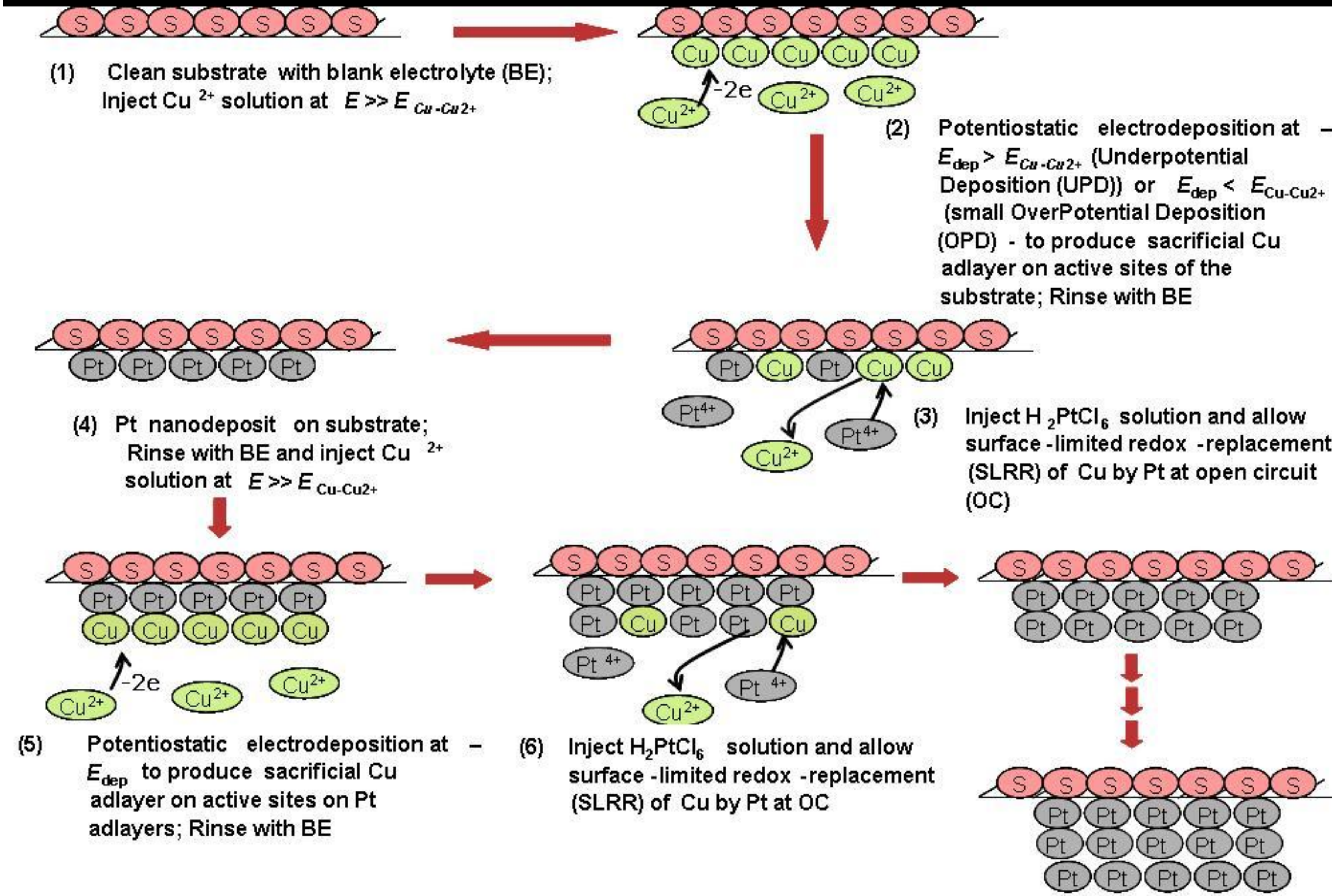
Advantages:

- 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

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



3.1.1 ECALD cont'd:

Noble-Metal: Pt, Pd (more abundant and cheaper than Pt)

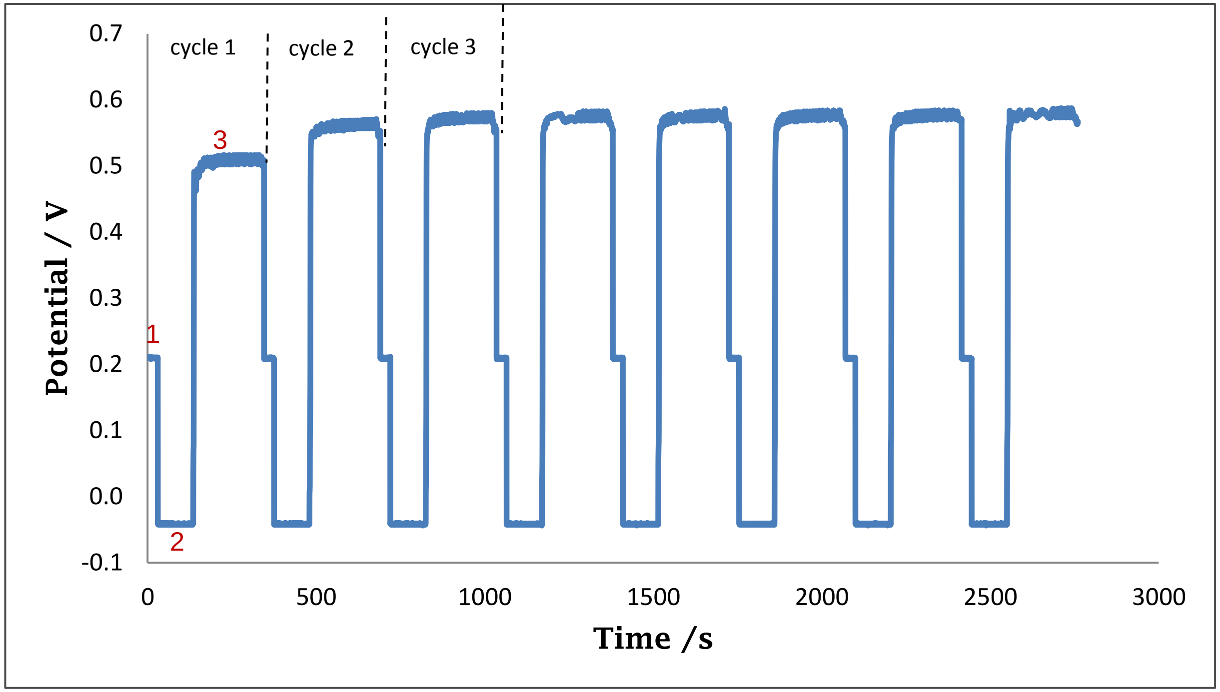
1mM $PdCl_2$ + Chloride as complexing agent
LB Sheridan et al., Langmuir 29 (2013) 1592

Substrate: Fuel Cell Carbon paper
- small OPD

Repeat cycles: Optimal 8X- monometal,
Pd8Pt8, Pt8Pd8,
Pd16Pt16, Pt16Pd16,
Pd16Pt8
16 PdPt co-deposition

T.S.Mkwizu, M.K. Mathe, and I. Cukrowski, ECS Trans. 19, 97-113 (2009)
T.S.Mkwizu, M.K. Mathe, and I. Cukrowski, Langmuir, 26, 570 - 580 (2010)
T.S Mkwizu, M.R. Modibedi, and M. K. Mathe, 219th ECS Meeting (2011)
Modibedi et al., ECS Trans. 50 (21) 2013
Modibedi et al., Electrochim.Acta 128 2014

Time-Potential curves



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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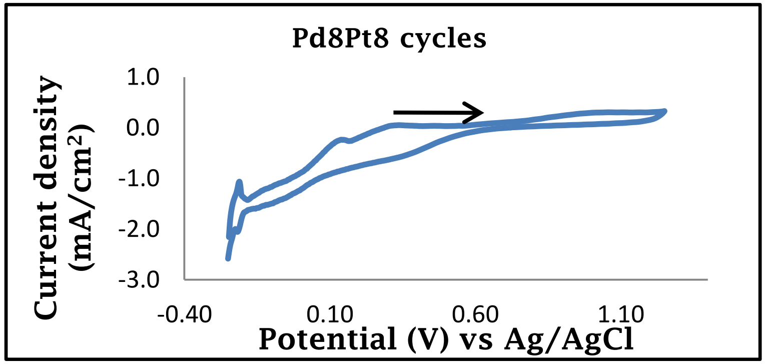
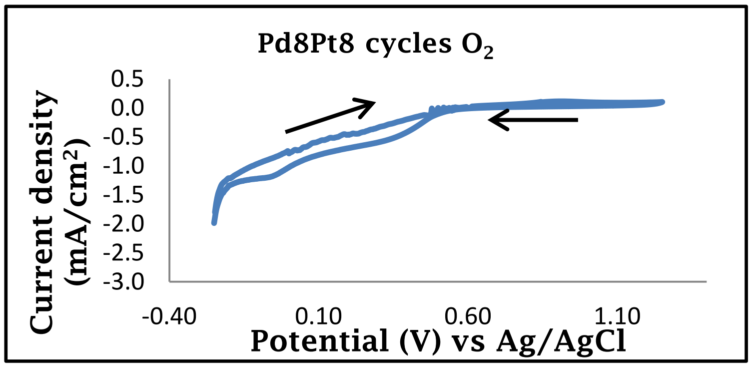
PdPt: Morphology and electrochemical evaluation



(i) 0.1 M HClO4 + N_2



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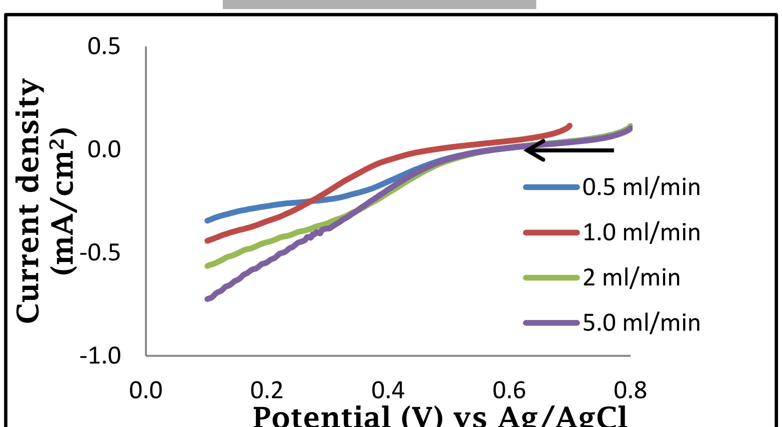
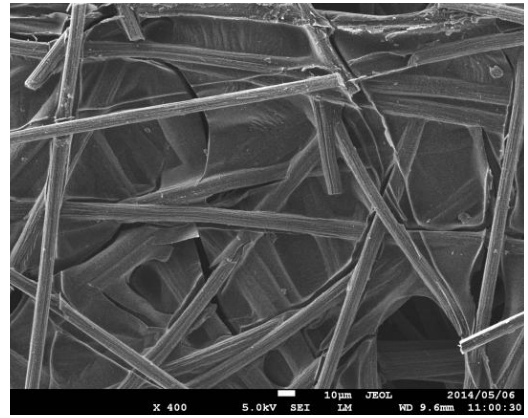
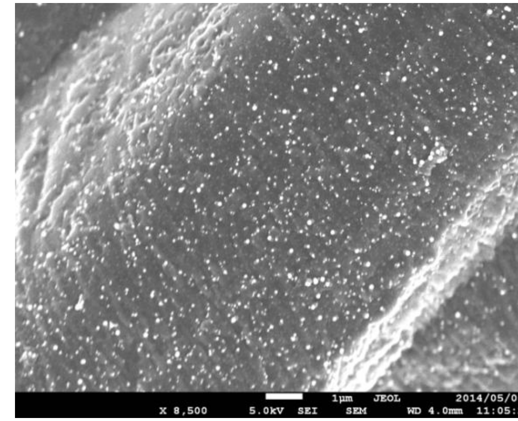
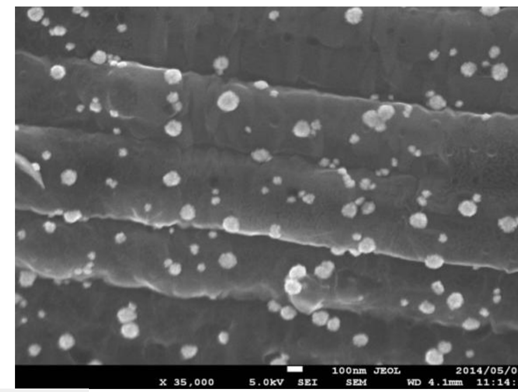
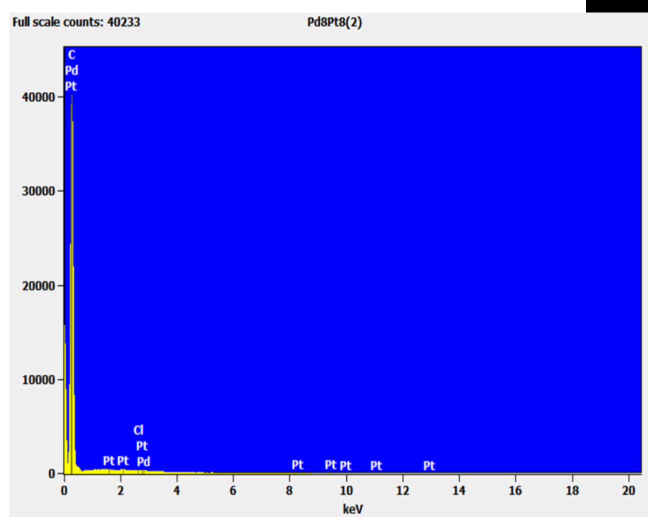


(iii) Current-Potential curves









PdL, PtM

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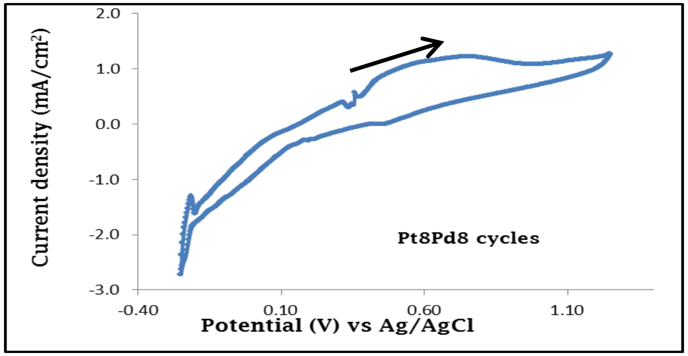
PtPd: Morphology and electrochemical evaluation



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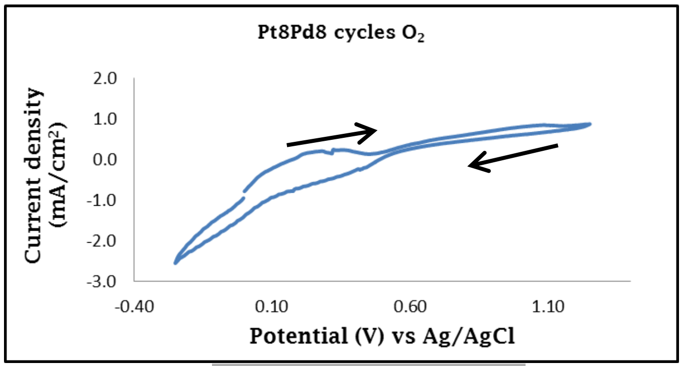

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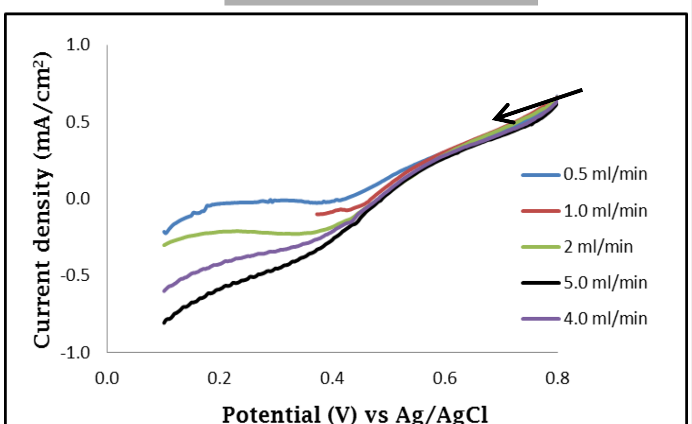

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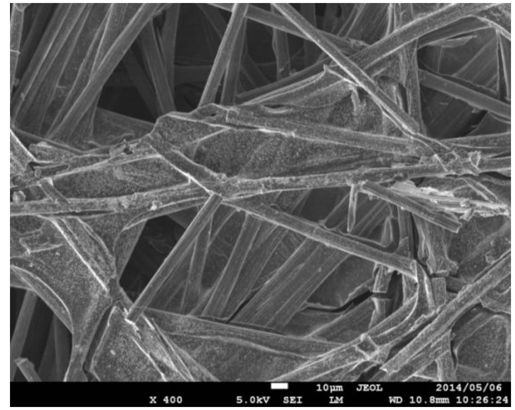

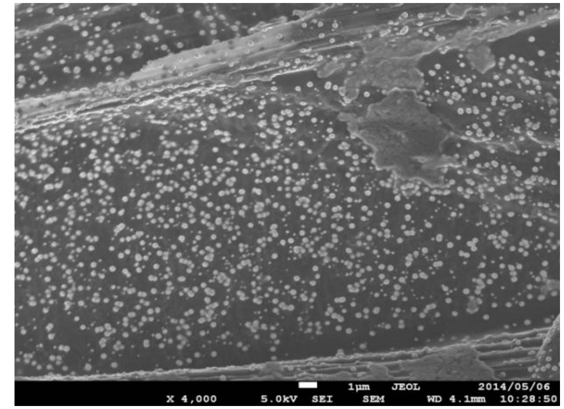

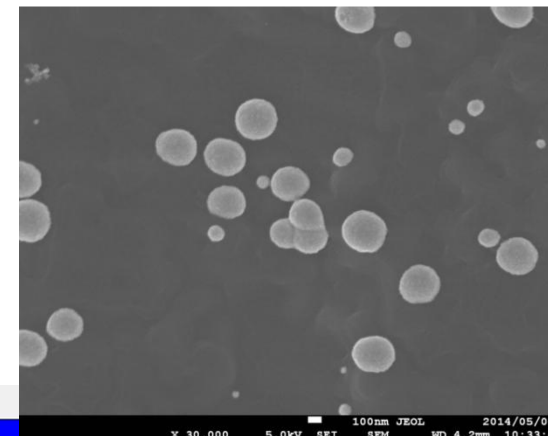

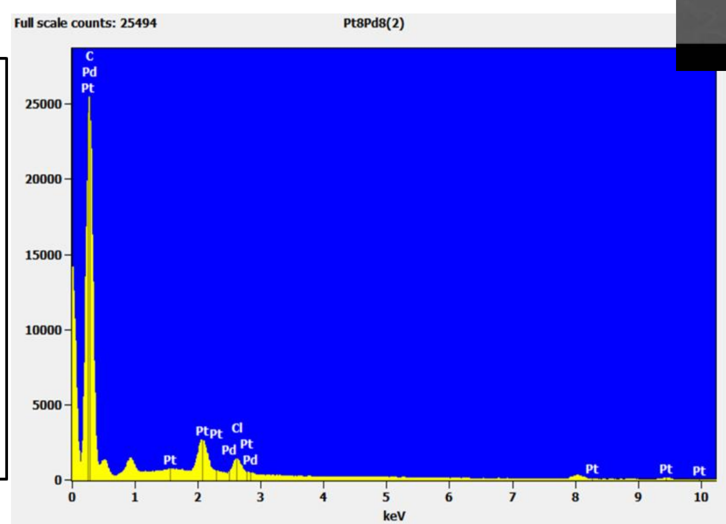

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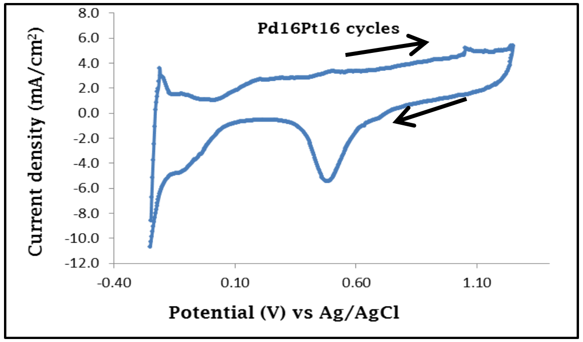
PdPt: Morphology and electrochemical



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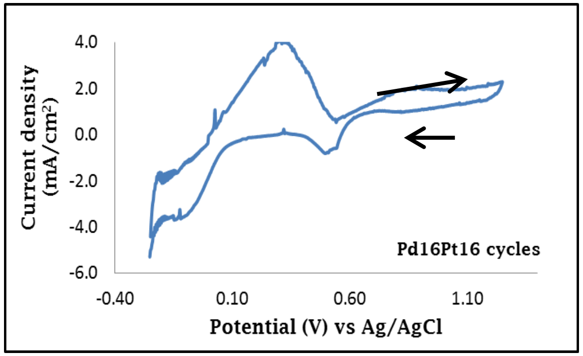

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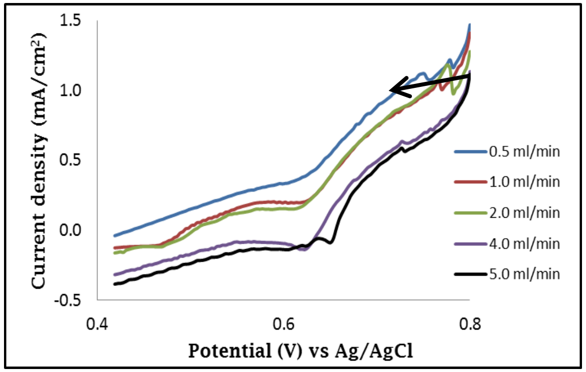

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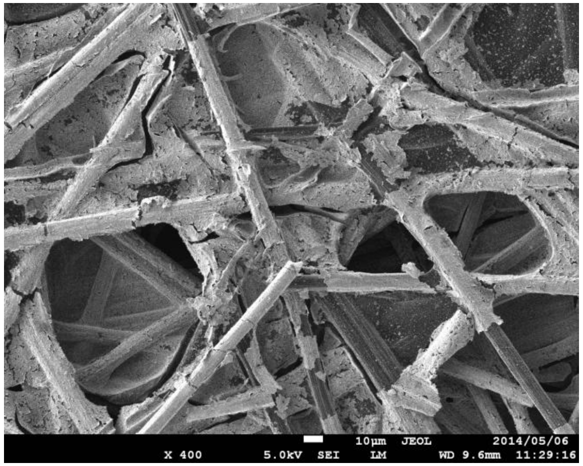

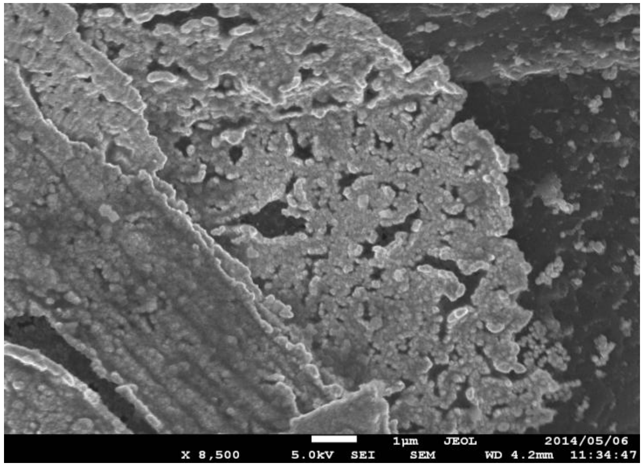

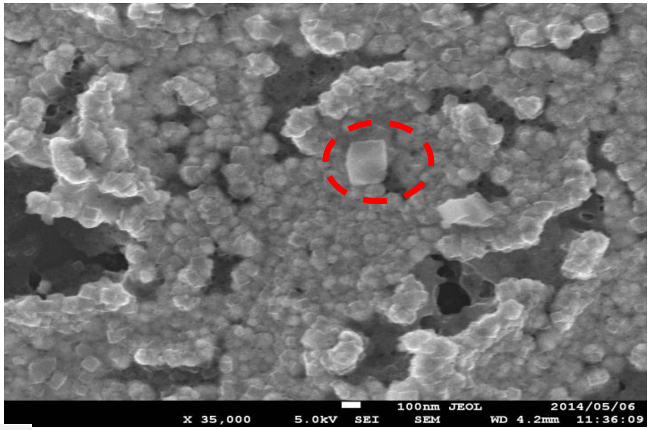

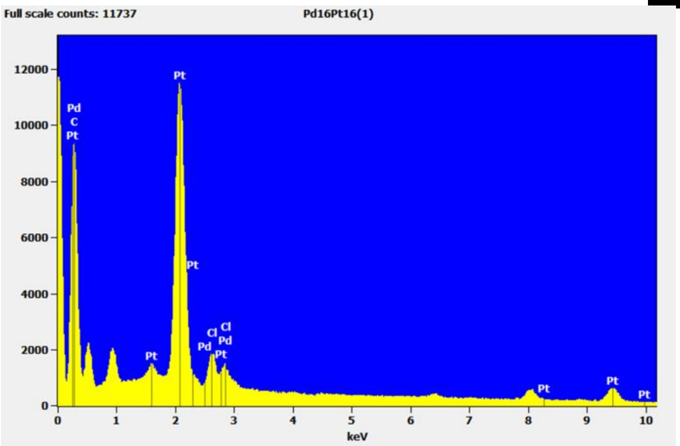

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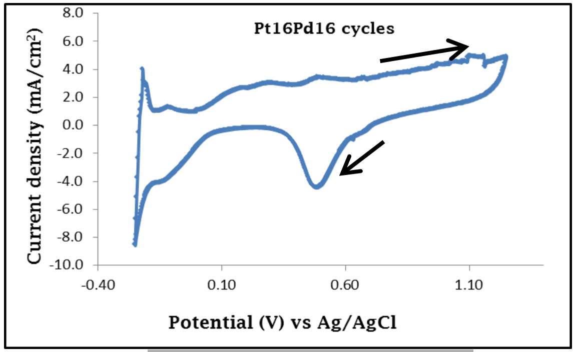
PtPd: Morphology and electrochemical evaluation



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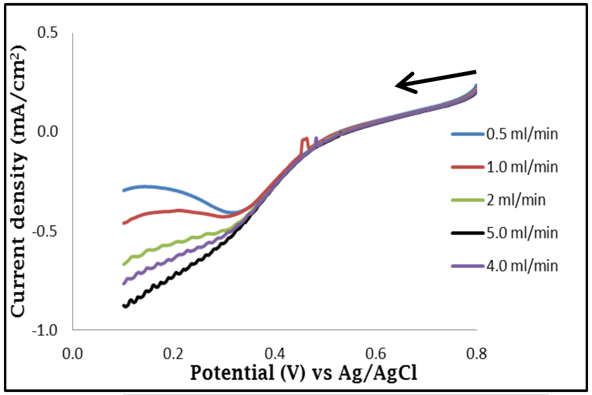

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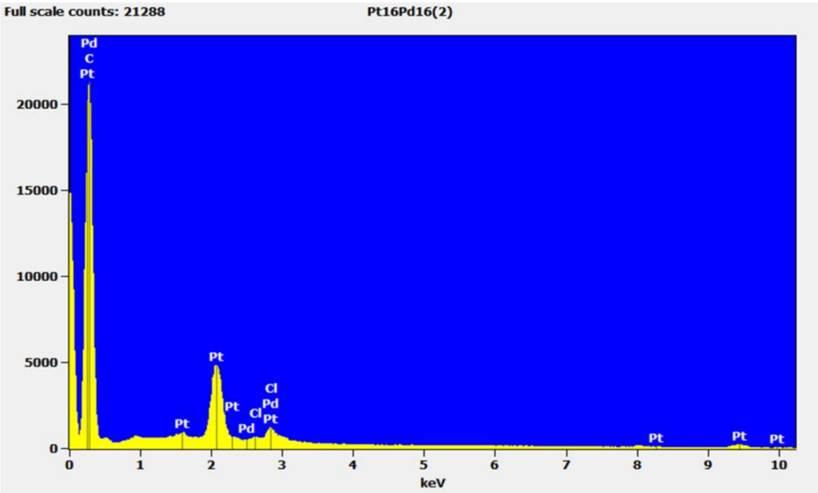

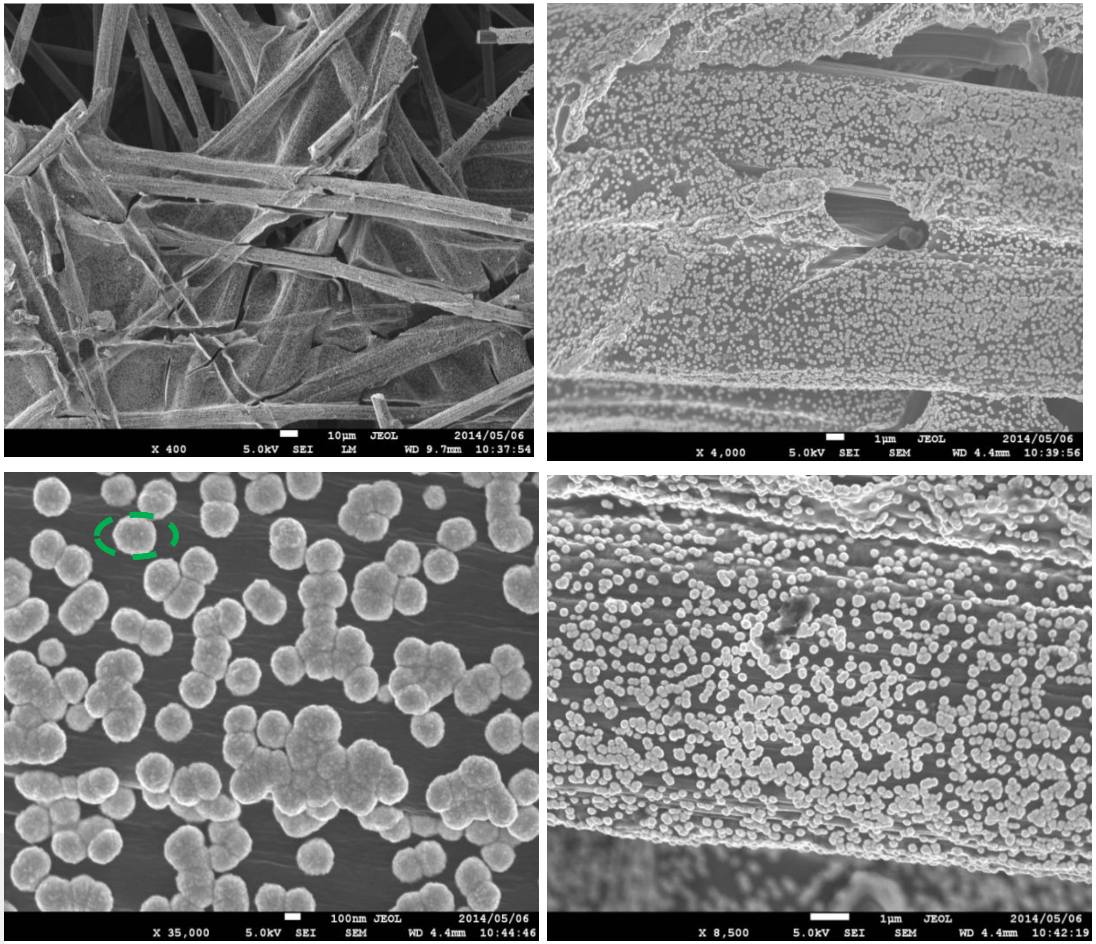

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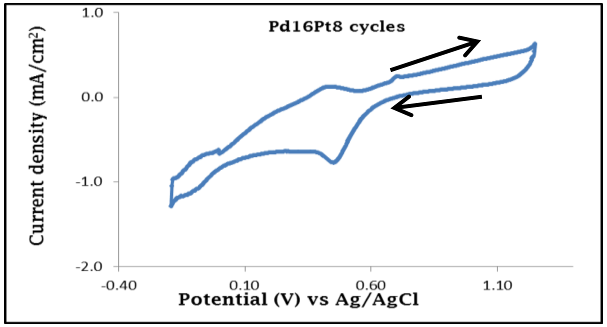
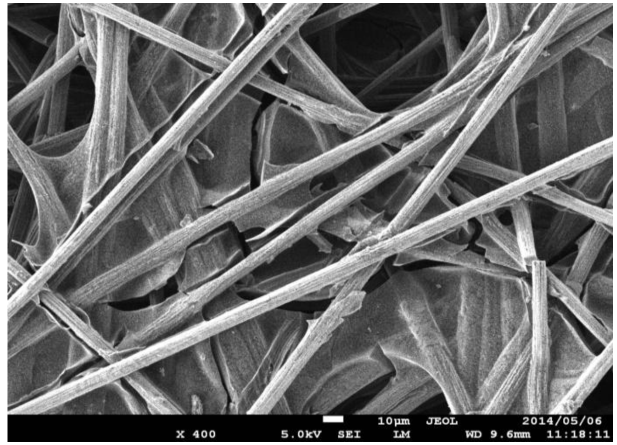
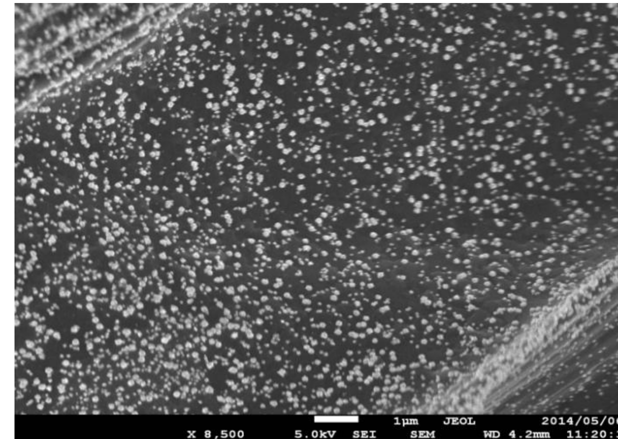
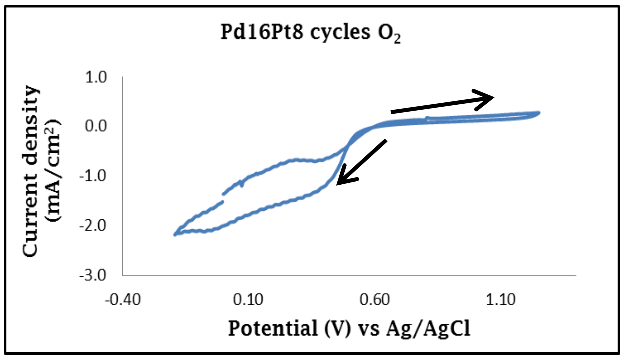
PdPt: Morphology and electrochemical evaluation



(i) 0.1 M $HClO_4 + N_2$







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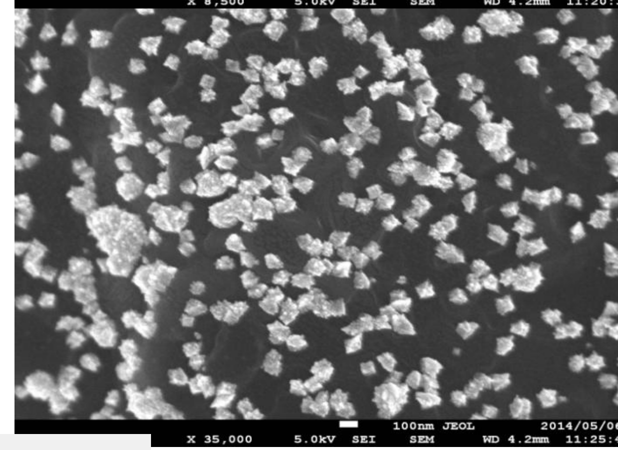

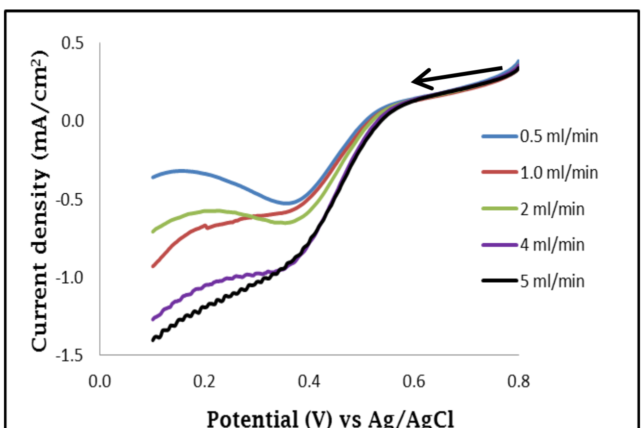

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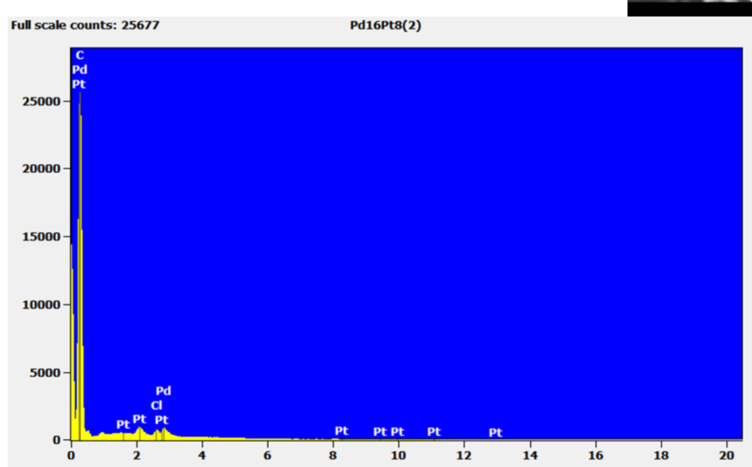

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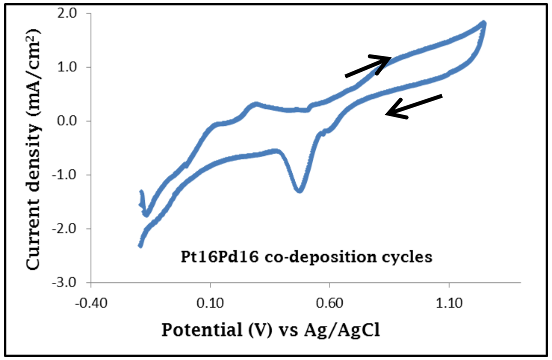

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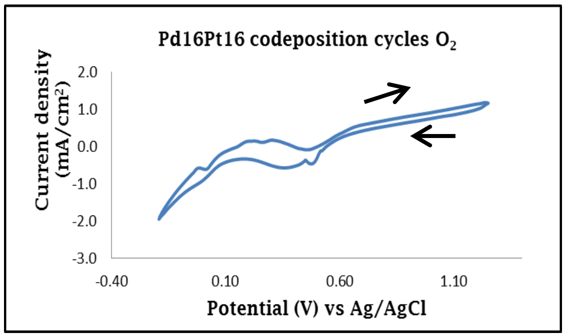

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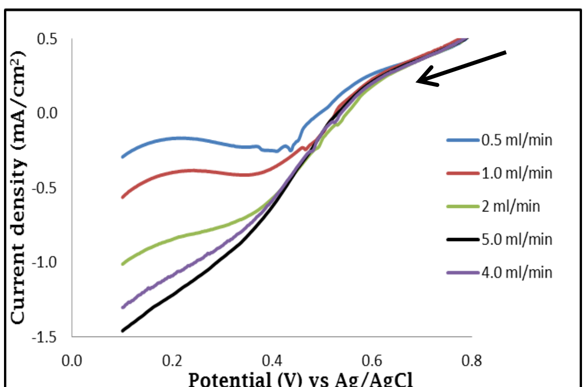

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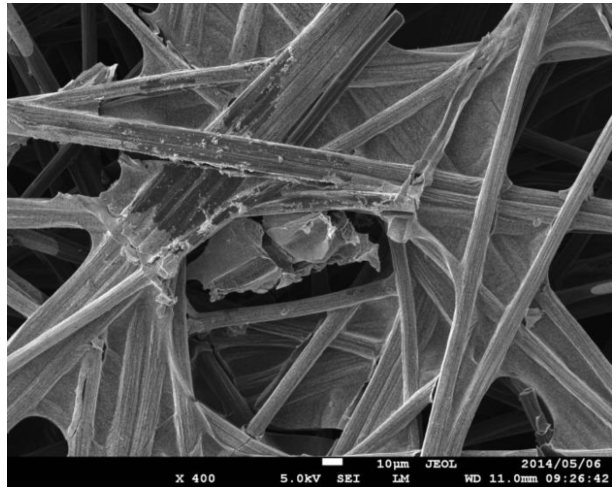

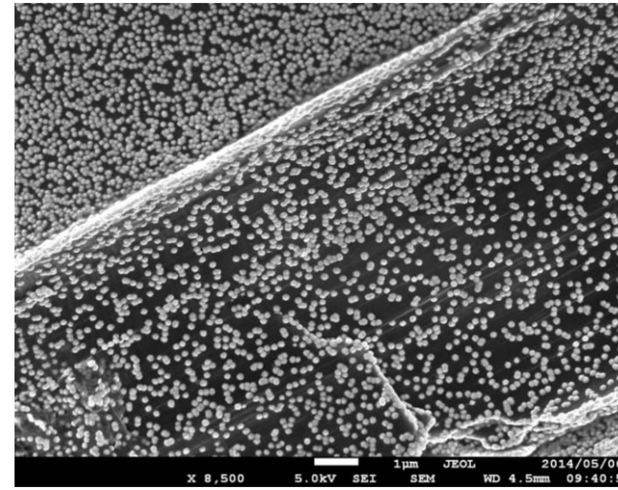

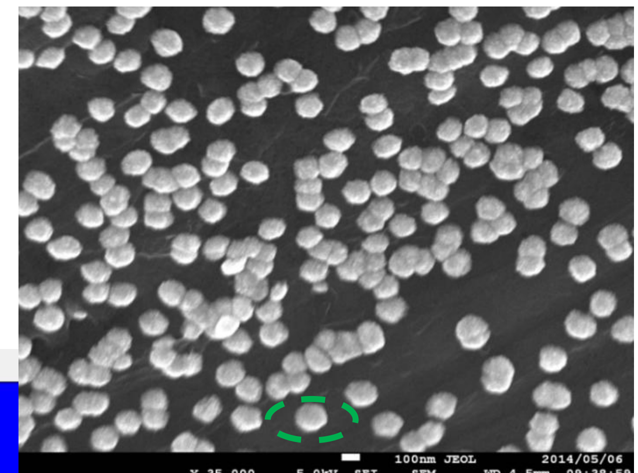

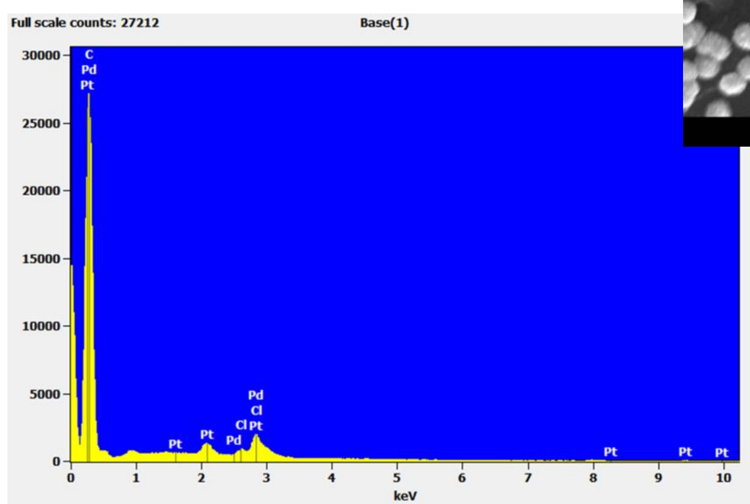

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Conclusions

Electro-Catalyst	Onset potential (V) vs Ag/AgCl	Max. current density (mA/cm²)
Pd 8x	0.504	0.5415
Pt 8x	0.548	0.2892
Pd8Pt8	0.546	0.6123
Pt8Pd8	0.584	0.6369
Pd16Pt16	0.582	0.8801
Pt16Pd16	0.725	1.3538
Pd16Pt8	0.581	1.2431
16 PdPt* co-deposition	0.566	1.3477

- Different structural shapes were observed - sequence

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Future Work

- Investigate catalyst tolerance to alcohol (methanol, ethanol)

- Optimization of Pd: Pt ratio that will give same or better performance than Pt

- MEA fabrication and FC testing under active conditions

- Explore the addition of 3rd metal to PdPt catalyst: Ni, Co

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THANK YOU