MSM ENERGY MATERIALS

Fuel Cell Catalysts and Membrane Development at the CSIR

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Outline of the presentation

- Overview of the CSIR
- Overview of Material Science and Manufacturing (MSM)
- Overview of Energy Materials (EM)
- Fuel cell (FC) research activities
- Membrane development
- Electrocatalysis
- MEA Fabrication: new developments
- Future Work

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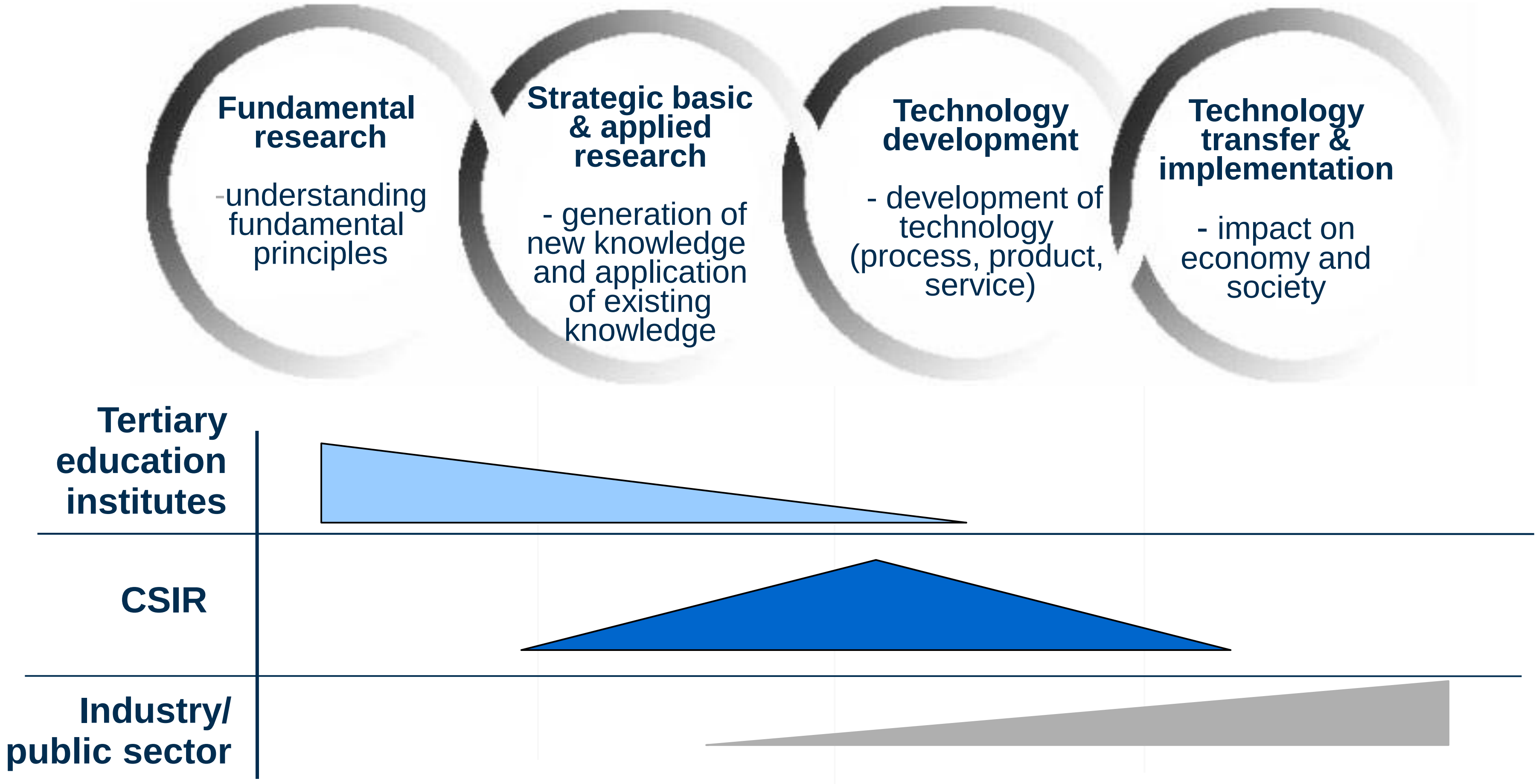
Strategic position in the National System of Innovation



The CSIR spans the research and innovation value chain but its role is differentiated from TEIs and industry/public sector

CSIR sites, people and financials

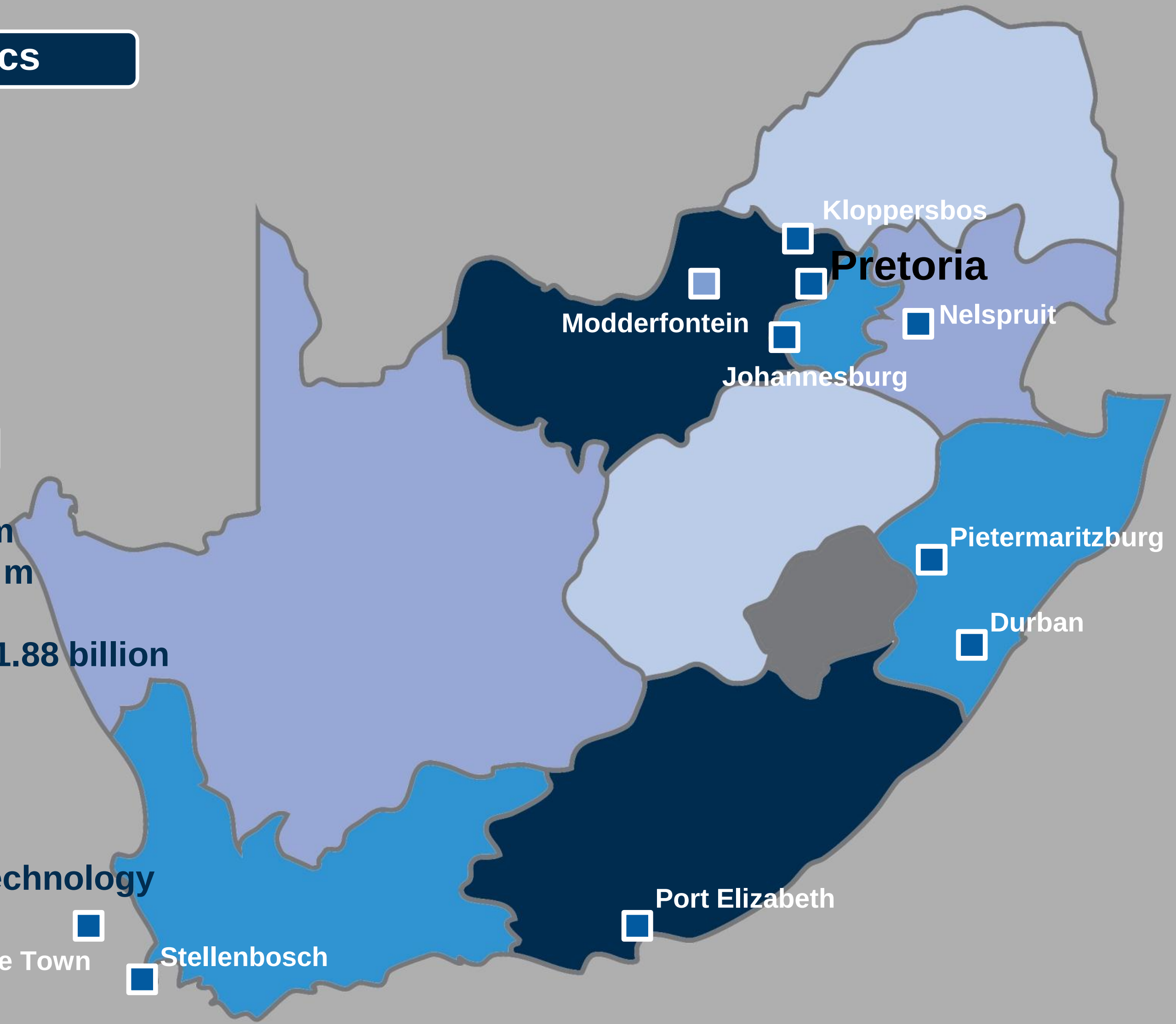
People and demographics

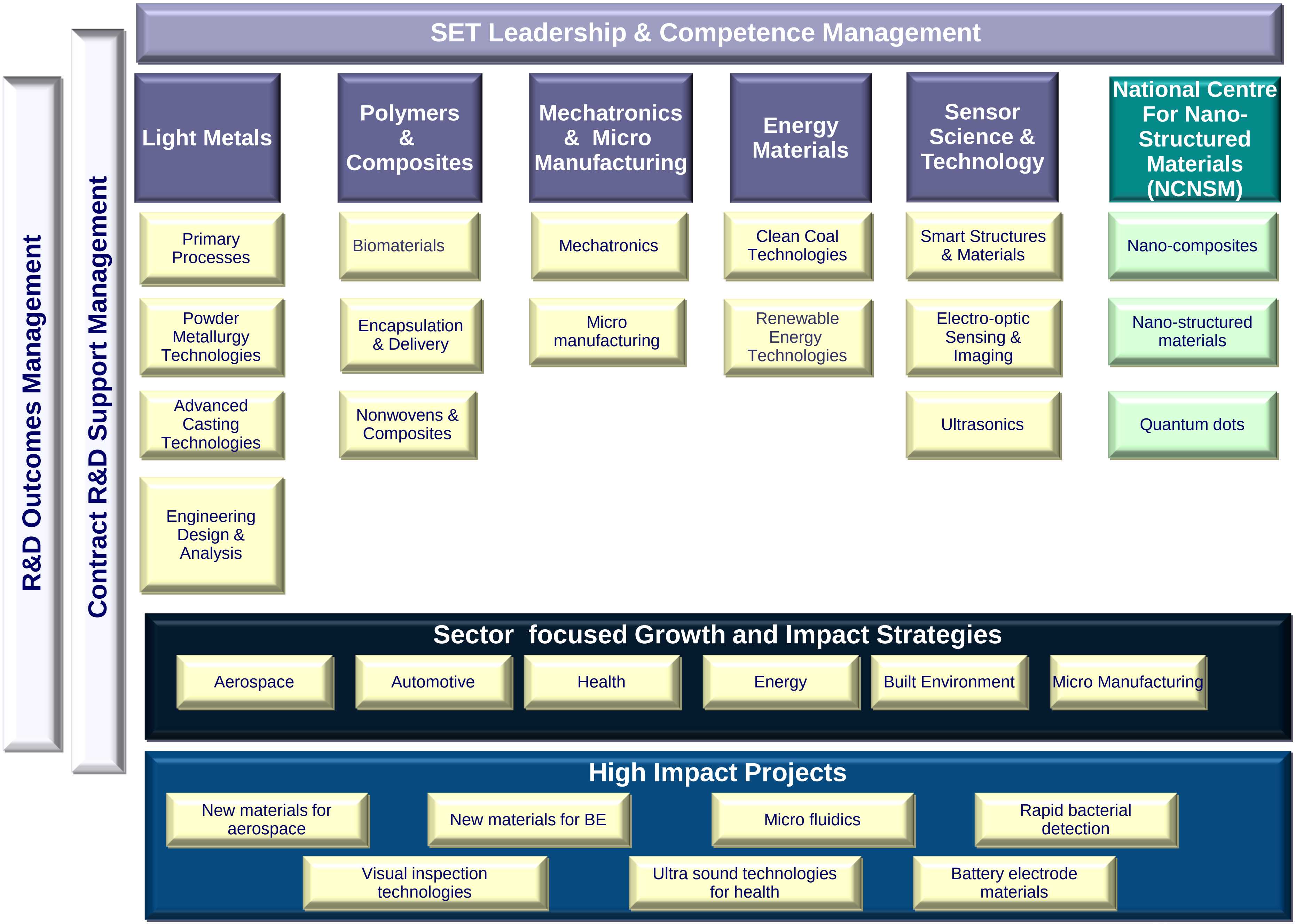
- 2370 members of staff
- 1537 in SET * base
- 299 with Doctorates
- 475 with Master's
- 54% of SET base black
- 34% of SET base female

Financials

- Contract Income: R1 273 m
- Parliamentary Grant: R557 m
- Royalties: R10 m
- Total operating income: R1.88 billion

*SET: Science, engineering and technology




R&D Outcomes Management
Contract R&D Support Management
SET Leadership & Competence Management
Light Metals
Primary Processes
Powder Metallurgy Technologies
Advanced Casting Technologies
Engineering Design & Analysis
Polymers & Composites
Biomaterials
Encapsulation & Delivery
Nonwovens & Composites
Mechatronics & Micro Manufacturing
Mechatronics
Micro manufacturing
Energy Materials
Clean Coal Technologies
Renewable Energy Technologies
Sensor Science & Technology
Smart Structures & Materials
Electro-optic Sensing & Imaging
Ultrasonics
National Centre For Nano-Structured Materials (NCNSM)
Nano-composites
Nano-structured materials
Quantum dots
Sector focused Growth and Impact Strategies
Aerospace
Automotive
Health
Energy
Built Environment
Micro Manufacturing
High Impact Projects
New materials for aerospace
New materials for BE
Micro fluidics
Rapid bacterial detection
Visual inspection technologies
Ultra sound technologies for health
Battery electrode materials

1. Fuel Cells

1.1 Fuel cell types: Low temperature PEMFC, DMFC

- **Membrane development:**
- Covalently cross-linked polyetheretherketone PEM for DMFC
- Incorporation of nanoparticles such ZrO_2 in Nafion membrane
- Characterisation: methanol crossover studies, conductivity tests, thermal stability
- MEA fabrication and testing (performance 10% less than Nafion membrane)

Luo et al., International Journal of Hydrogen Energy 34, 2009
Zheng et al., International Journal of Hydrogen Energy, 35(8), 2010,
Zheng et al.,Journal of Power Sources, 196 (3), 2011

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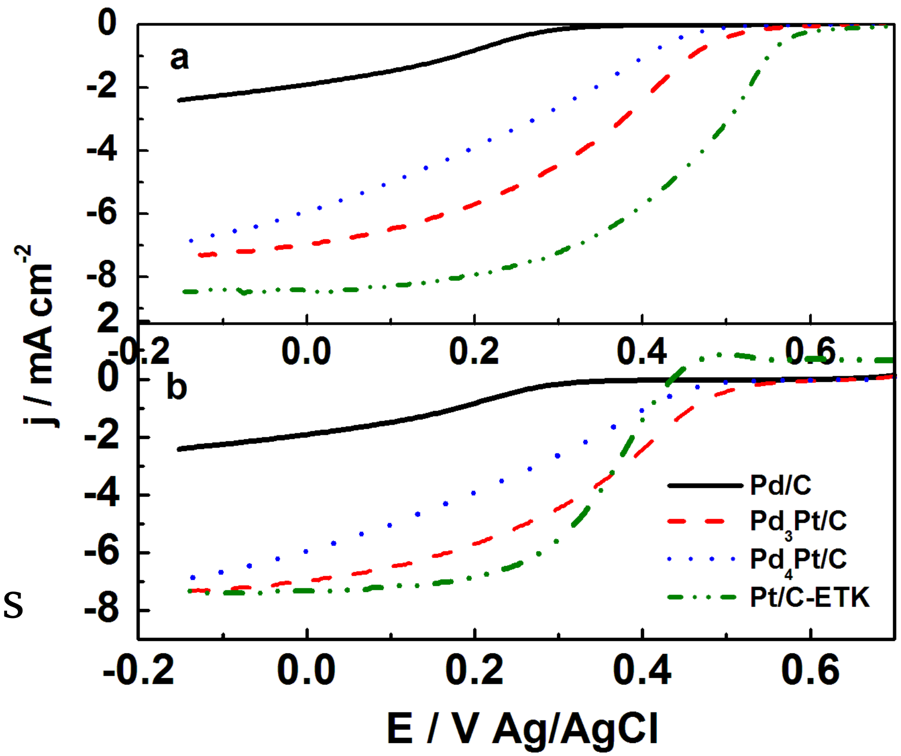
- # Electrocatalysts:
  - ## Oxygen reduction reaction (ORR):

(a) ORR in H_2SO_4
Best catalyst: **Pt**

(b) ORR in H_2SO_4 + MeOH
Potential drop-
~220mV: Pt catalyst
Max 58mV: Pd catalysts
No current drop: Pd-catalysts

Best catalyst: **Pd_3Pt/C**



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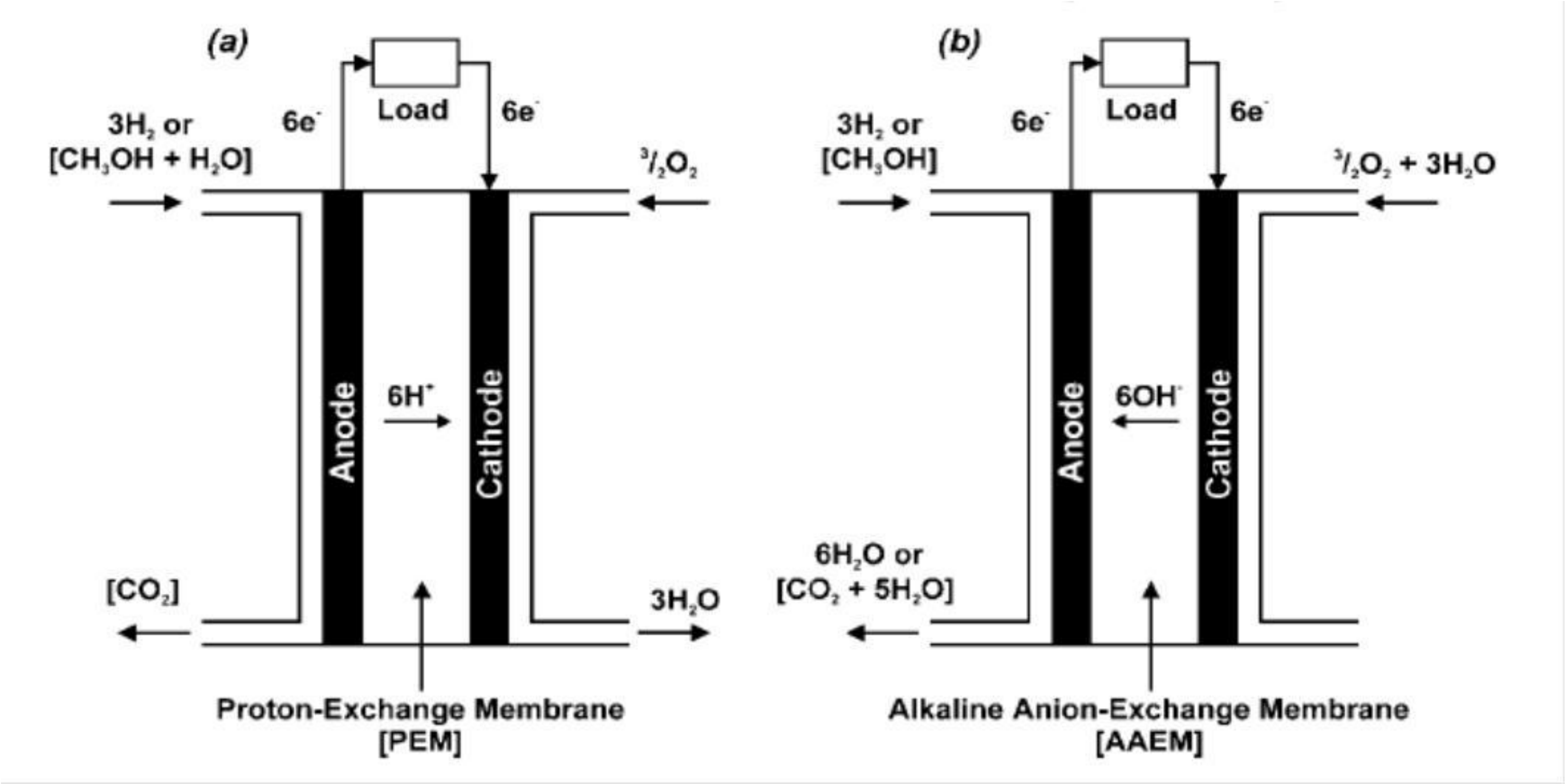
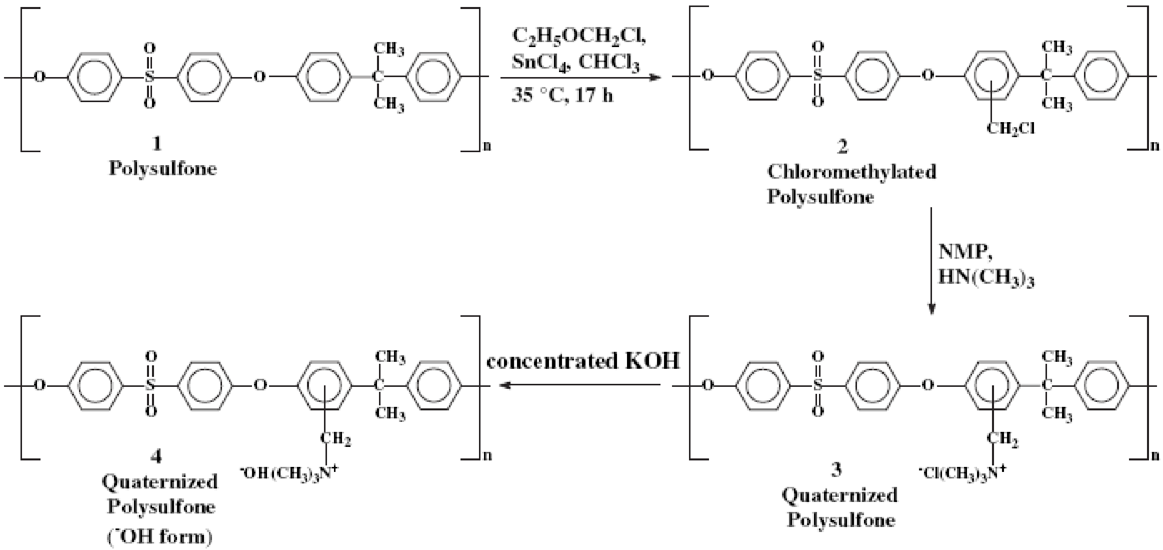
1.2 Anion exchange membrane: (DAFC)



Why AAEM?

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

Preparation of nano-composite membrane



Multi-step synthesis of quaternary polysulfone (QPSU)

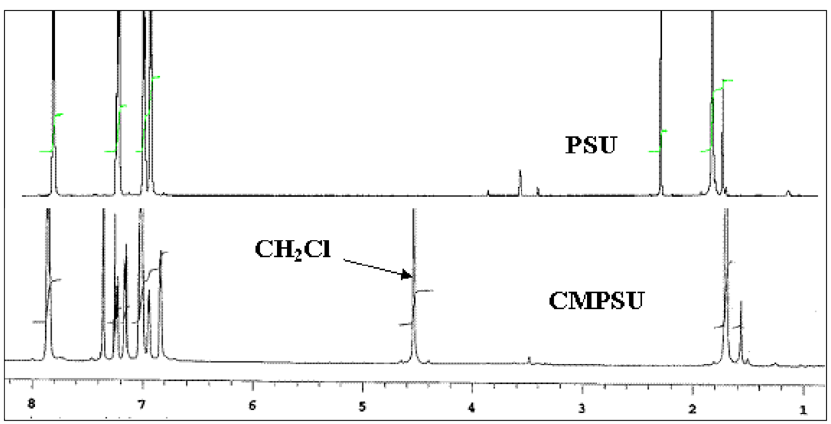
- The OH- form of QPSU was dissolved in DMAc and different proportion of TiO_2 nano filler was added to this solution and then stirred for 24 h, followed by casting.
- Dried at 80 °C overnight.

Avram *et al.* J macromol Sci Pure Appl Chem, A34 (1997) p1701

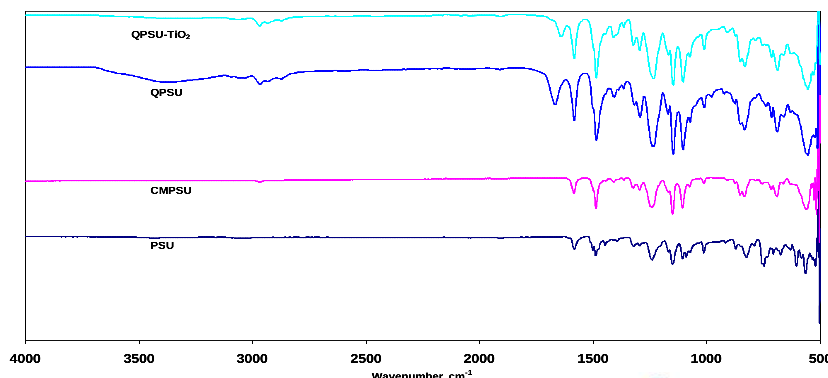
PNAS, vol 105 (2008) p20611

IJHE, vol 36 (2011) p7291

1. ¹H-NMR SPECTRA



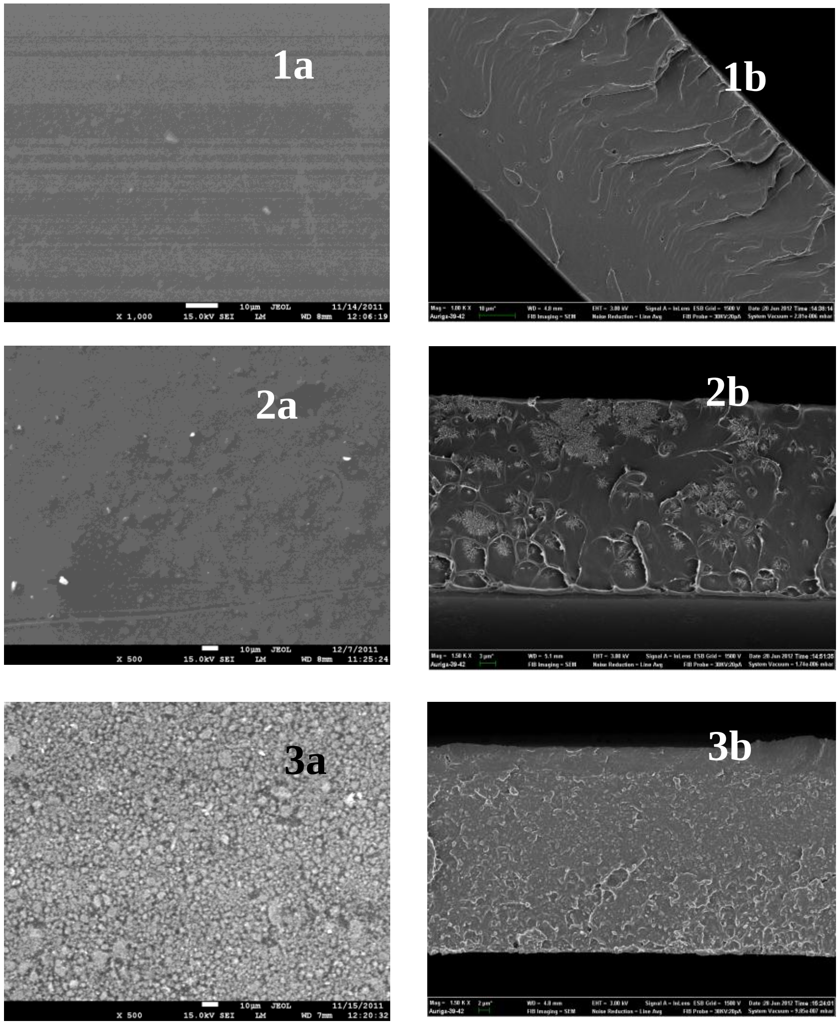
2. FT-IR SPECTRA



Abuin *et al.* IJHE, 35 (2010) p 5489.

Nonjola *et al.* IJHE, 38 (2013) p 5115

Membrane morphology



SEM images of surface and cross section (1) QPSU, (2) QPSU/2.5%TiO_2 and (3) QPSU/10%TiO_2.

- All membranes defect free surface
- QPSU shows a smooth and uniform (1a&b)
- TiO_2 particles are well dispersed in the membrane with 2.5% loading (2a&b).
- TiO_2 dispersion in 10% loading (3a&b) shows negligible agglomeration.
- This implies that prepared composite membranes can be expected to perform consistently in alkaline fuel cell

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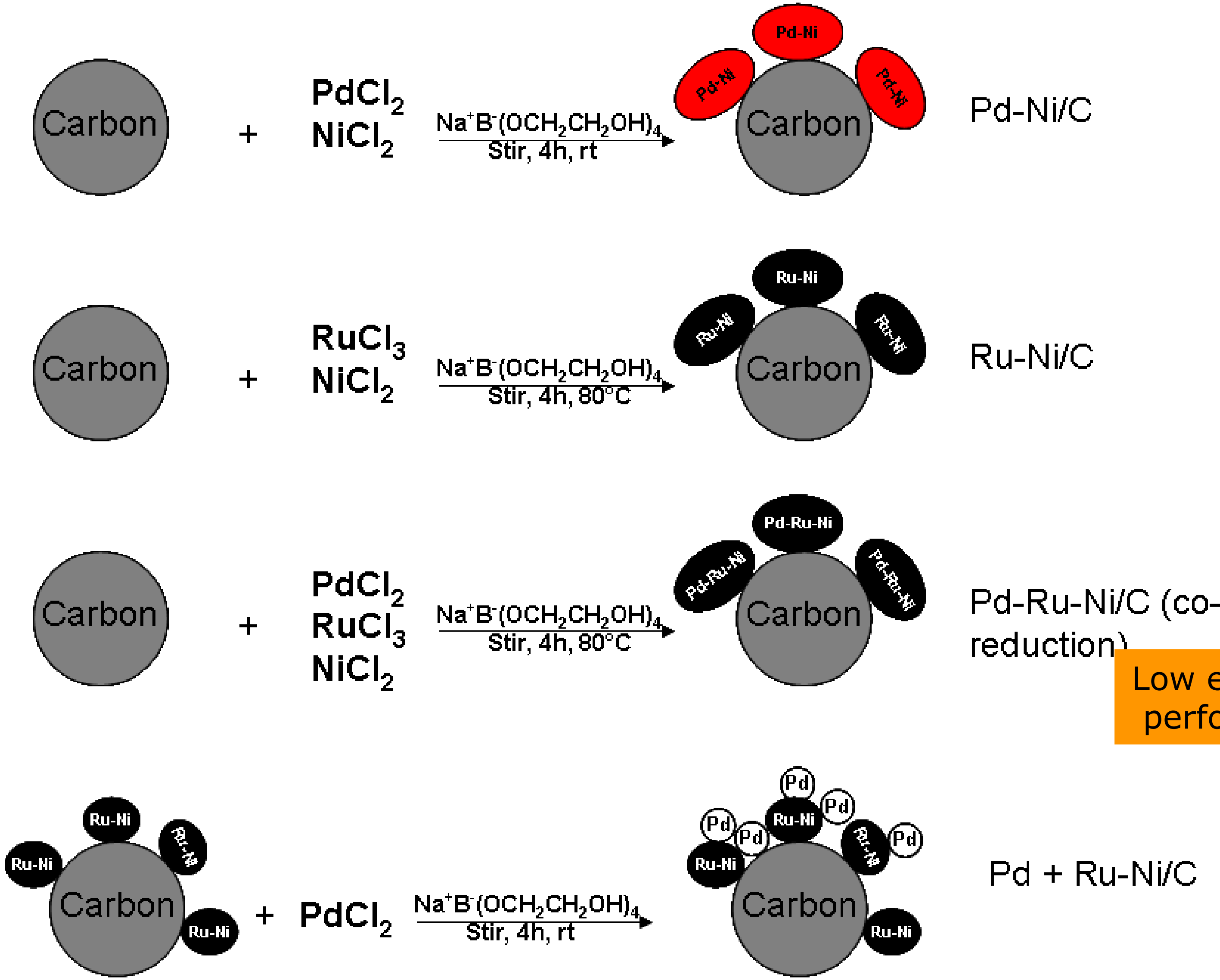
Nonjola *et al.* IJHE, 38 (2013) p 5115

• Electrocatalysts: Synthesis methods

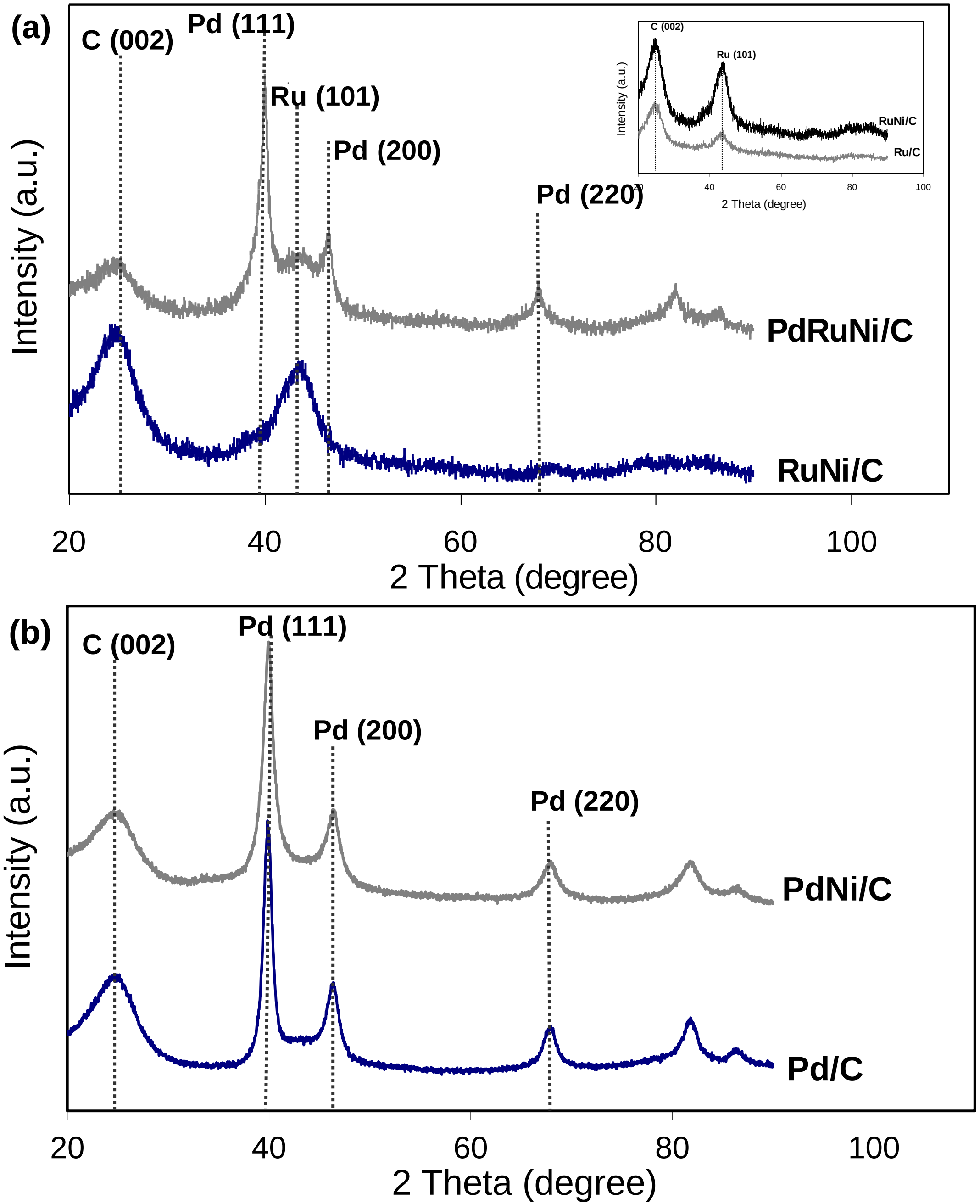
reducing agent: mixture $NaBH_4$ and ethylene glycol



Low ethanol oxidation performance vs Pd+Ru-Ni/C

Modibedi et al., International Journal of Hydrogen Energy, 36 (8) (2011) 4664,
Mathe et al., Energy Procedia 29 (2012) 401

XRD micrographs of nanocatalysts



no significant shift in peak: Ni did not alloy well with Pd using this preparation method at rt.

Ramulifho et al., Electrochim. Acta, 59 (2012) 310,
Ramulifho et al., J. Electroanal. Chem., 692 (2013) 26

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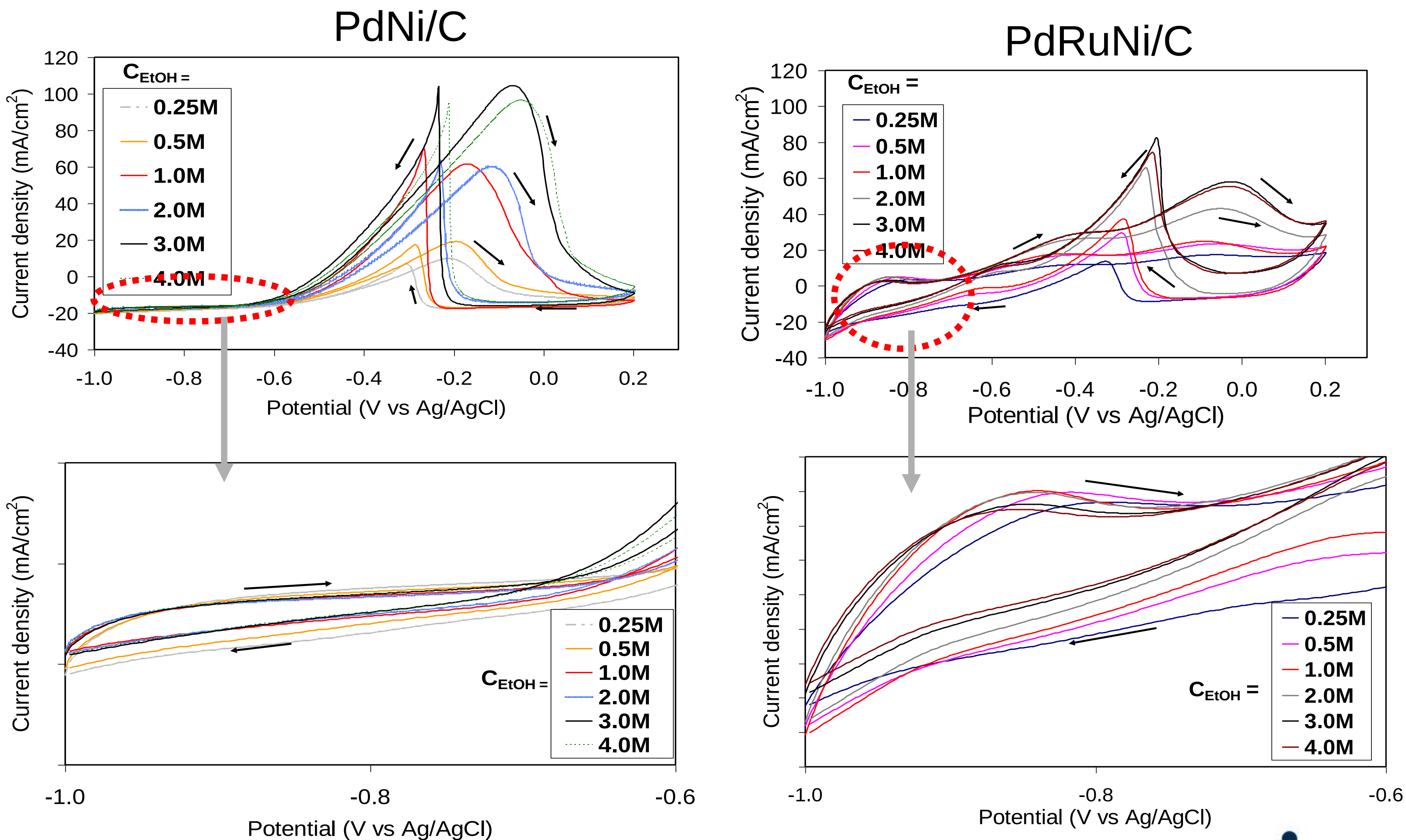
Effect of ethanol concentration on current



↑[EtOH] up to 3 M ↑coverage of the CH_3COads species on the nanocatalyst surface

Resulting in increase in current density

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Electro-catalyst performance: passive alkaline DEFC

Electro-catalyst	Open circuit voltage (V)	Power/total loading (mW/mgPd)
PdCeO2/C (ACTA-SpA)	0.795	3.1736
PdNi/C	0.653	3.1916
PdRuNi/C	0.768	2.5798
PdRuSn/C	0.623	0.2386

Cathode: 0.1mg/cm2 FeCo (ACTA-SpA)

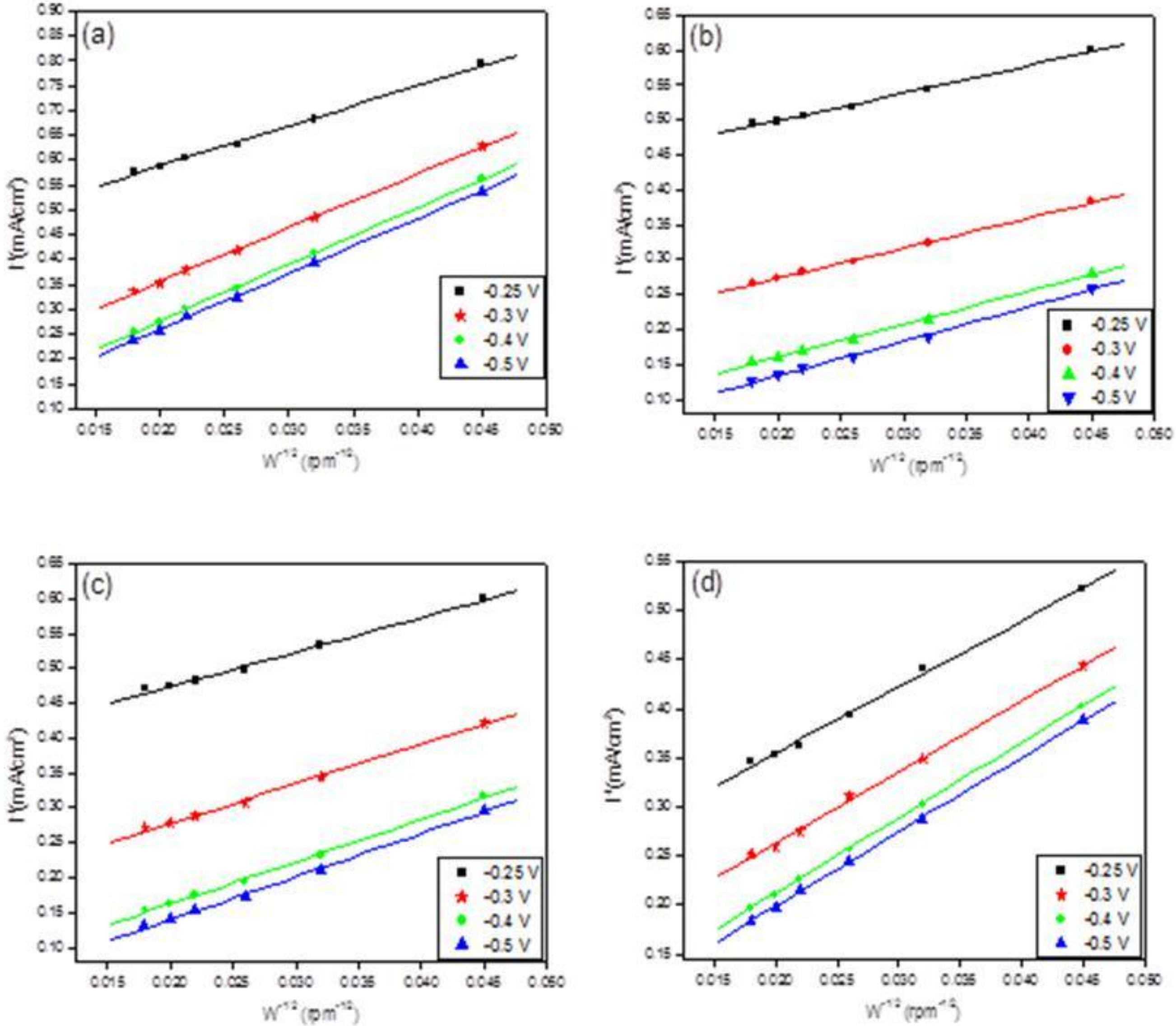
Electrocatalysts: Microwave-assisted polyol method

- Oxygen reduction catalysts

N-doped CNTs: thermal chemical vapour deposition

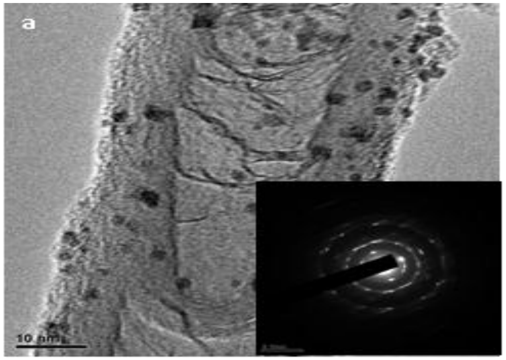
Ru/N-CNTs: microwave assisted reduction

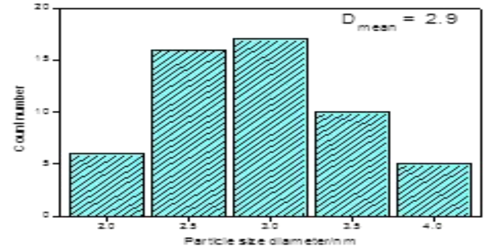
Koutecky-Levich plots

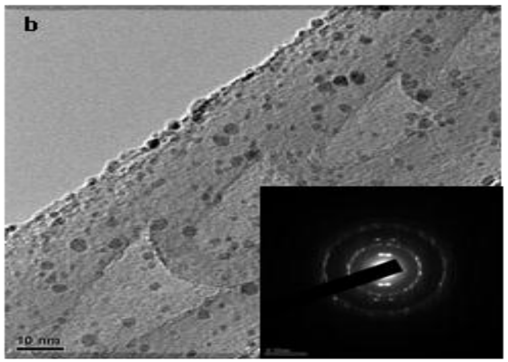


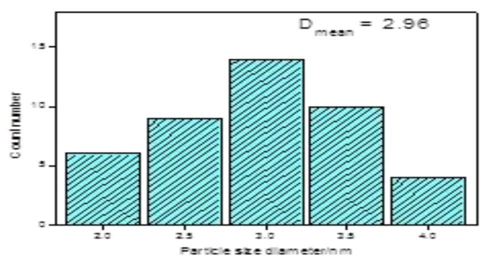
Mabena, Modibedi et al., Fuel Cells 12(5) (2012) 862

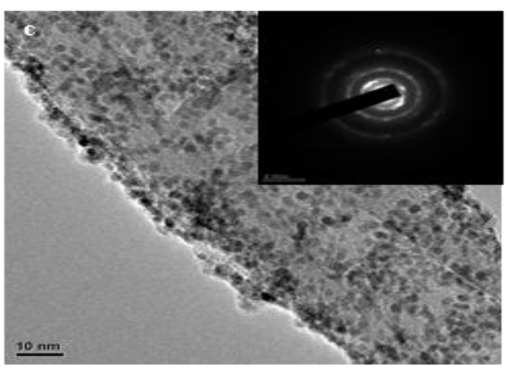
ORR catalysts characterization

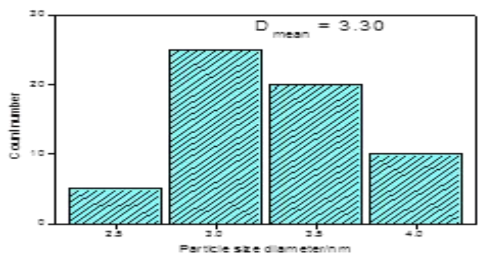












Electrode	Onset potential V	No of electron transferred at (1500 rpm, -0.30V)	Limiting current density (mA/cm^2)
N-CNTs	-0.166	2.4	-2.95
2Ru/N-CNTs	-0.158	3.9	-4.76
5Ru/N-CNTs	-0.153	3.7	-4.54
10Ru/N-CNTs	-0.148	3.2	-3.66

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- **Graphene oxide-MWCNT hybrid for Alcohol oxidation reaction in alkaline electrolyte**

Supported Pd and PdNi

Electrocatalysts: Electrochemical Atomic Layer Deposition technique (ECALD)

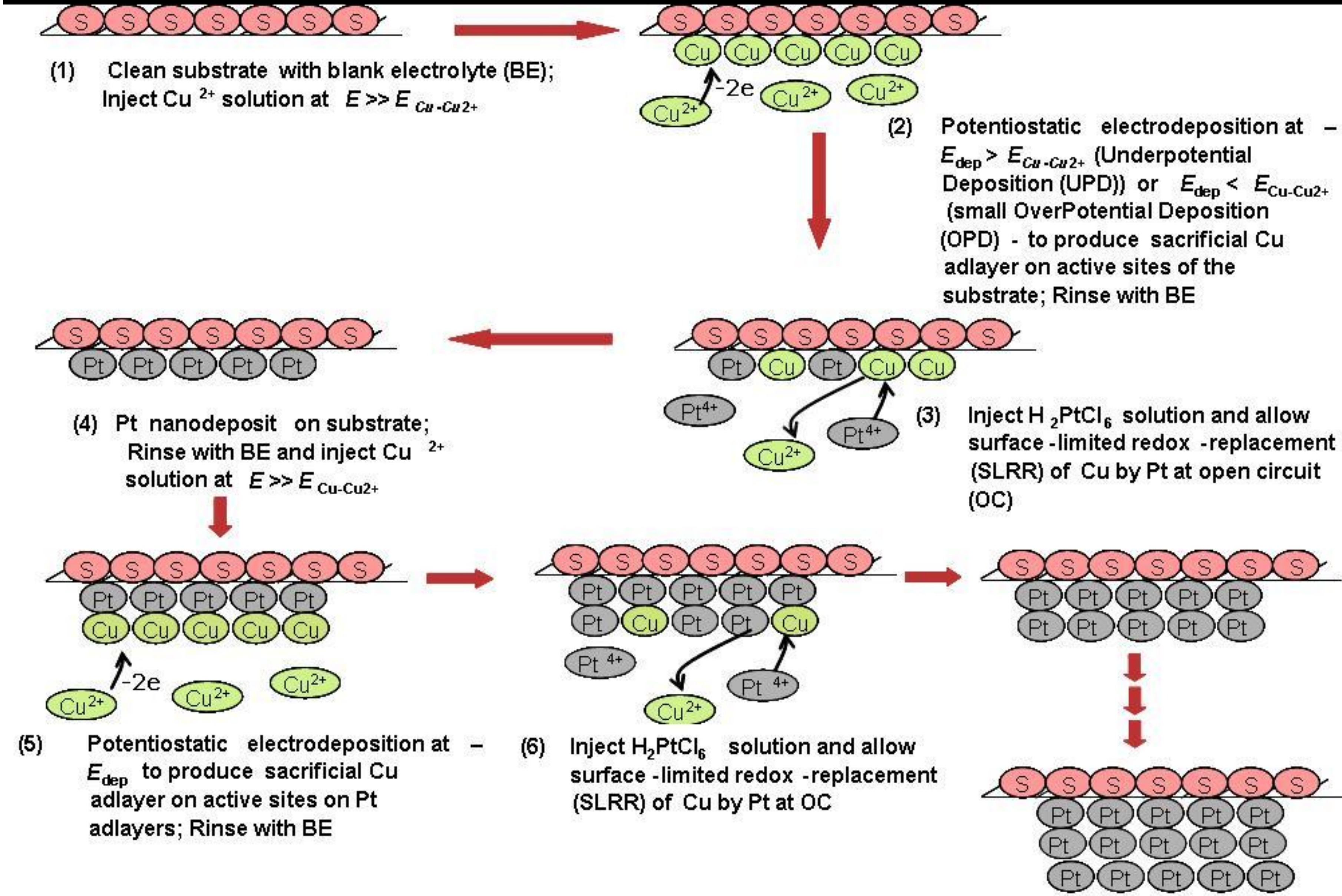
Definition:
alternated electrodeposition of atomic layers of elements on a substrate, employing under-potential deposition (UPD) in which one element deposits onto another element at a voltage prior to that necessary to deposit the element onto itself

Advantages:

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

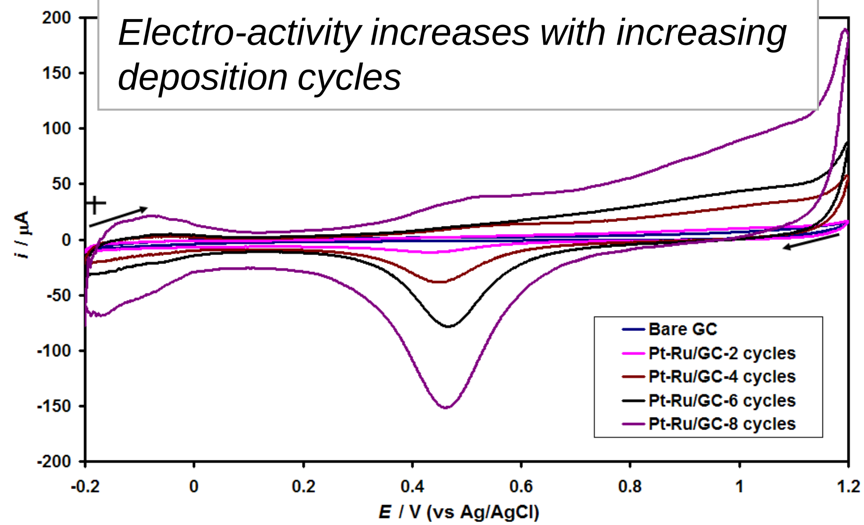
Offers atomic layer control- fundamental for controlled growth processes

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

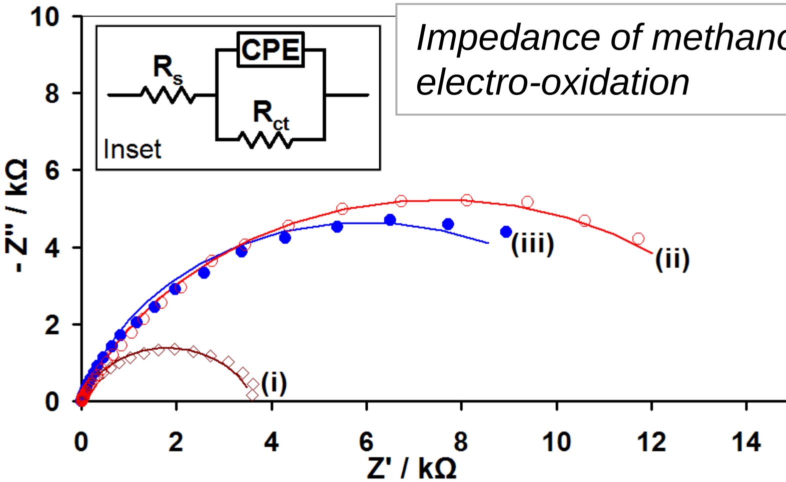


Tuning Electrocatalysis using sequential electrodeposition…

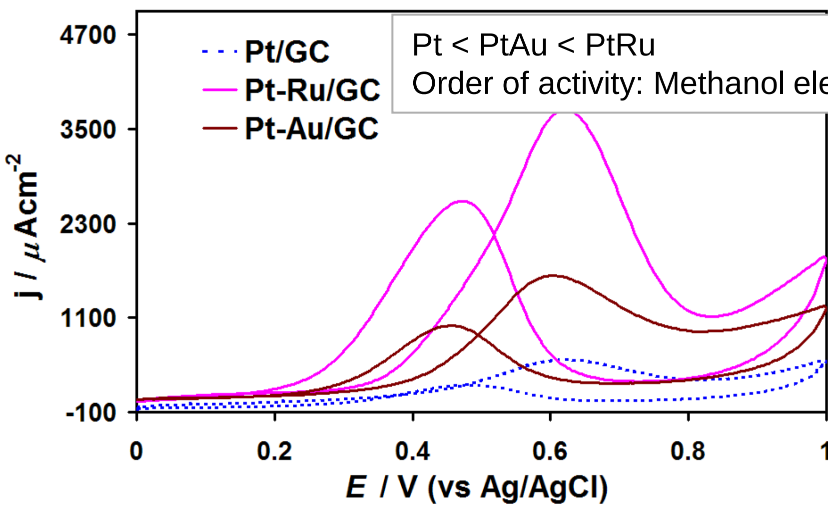
Electro-activity increases with increasing deposition cycles

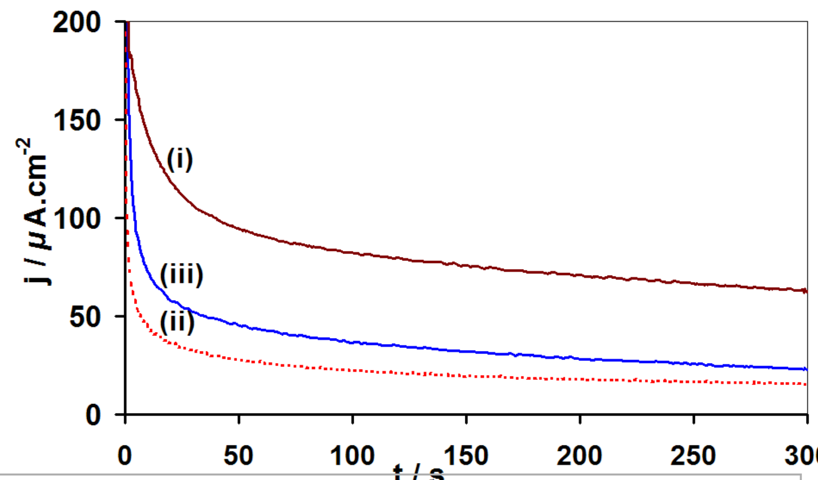


Impedance of methanol electro-oxidation



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

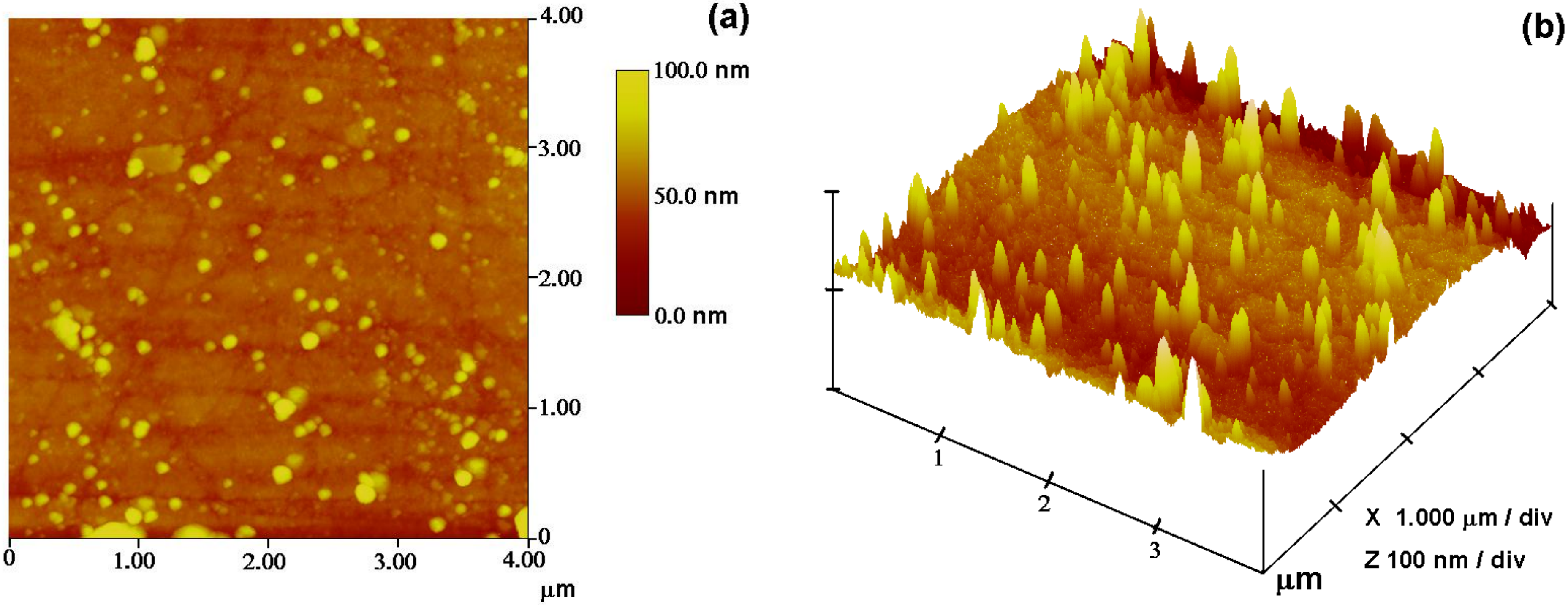




(i) Sequentially-deposited with Cu SLRR bimetallic PtRu / GC
(ii) Sequentially- *codeposited* with Cu SLRR bimetallic Pt-Ru/GC
(iii) Sequentially-deposited with Cu SLRR monometallic Pt/GC

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 using sequential electrodeposition...



AFM images of Pt|Ru nanoparticles obtained after 8 deposition cycles with Cu SLRR

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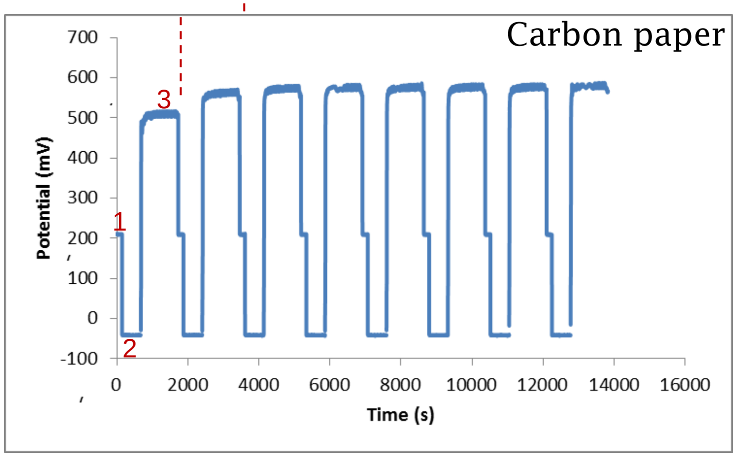
2.3 Membrane Electrode Assembly (MEA)

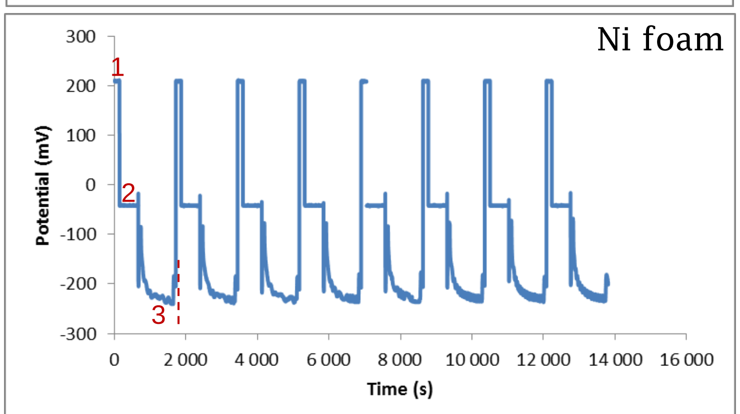
Noble-Metal: Pt, Pd

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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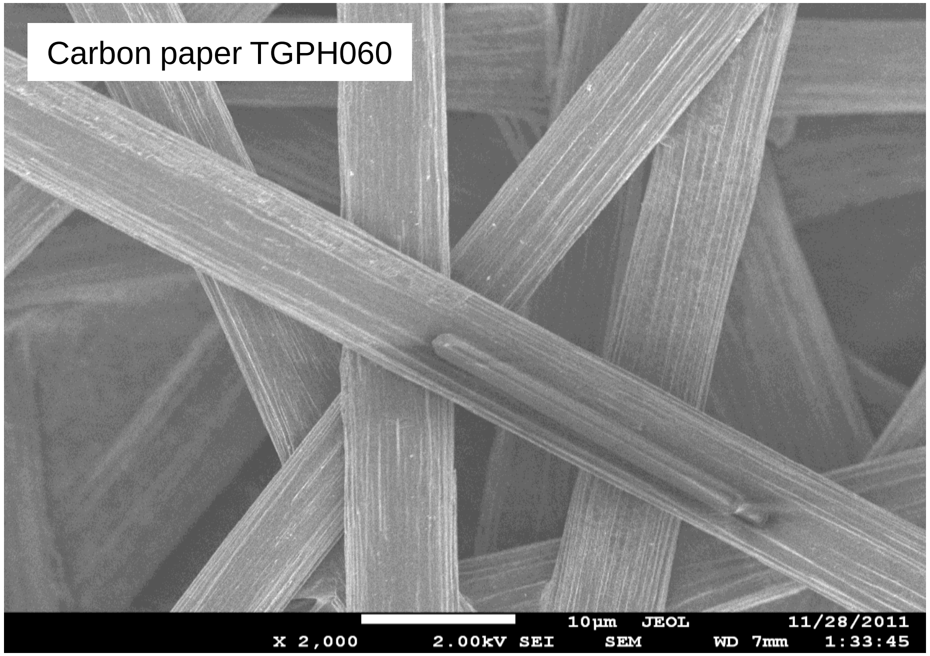
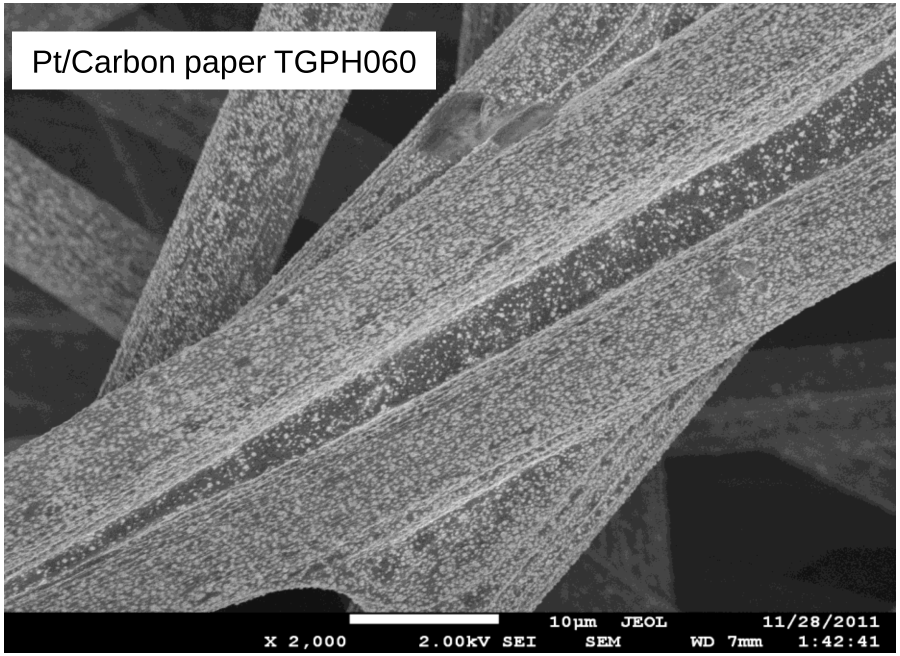
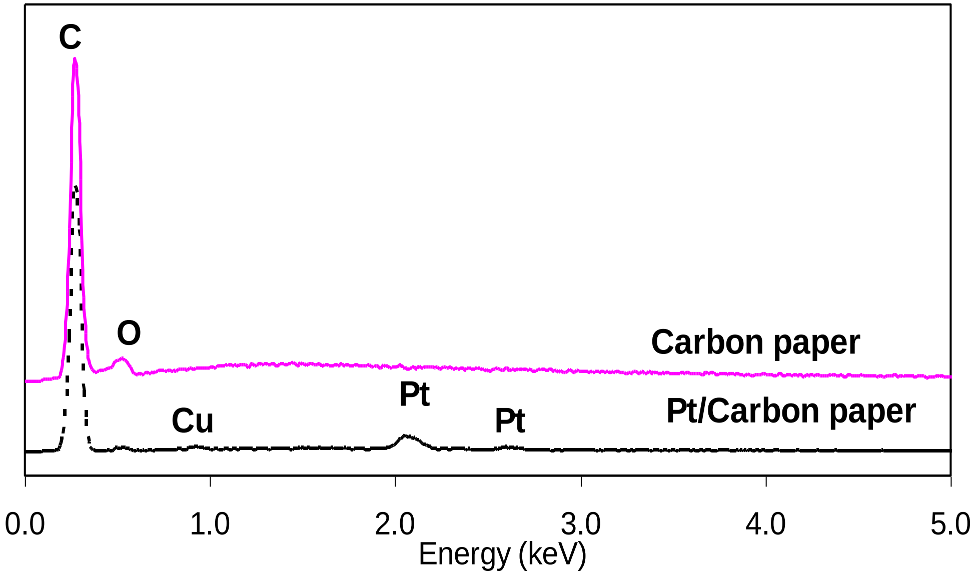
Modibedi et al., ECS Trans. 50, 2013

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







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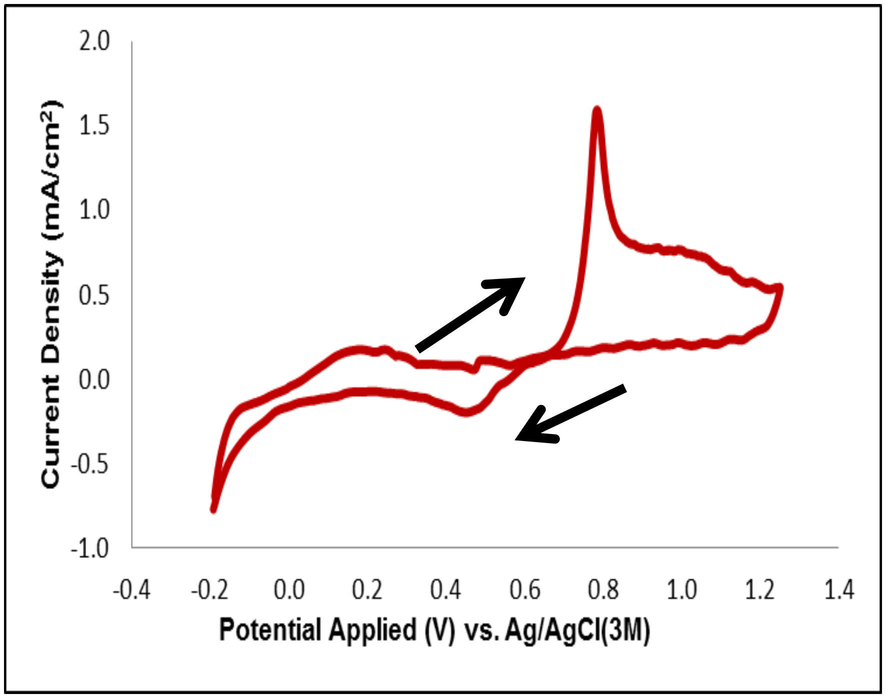
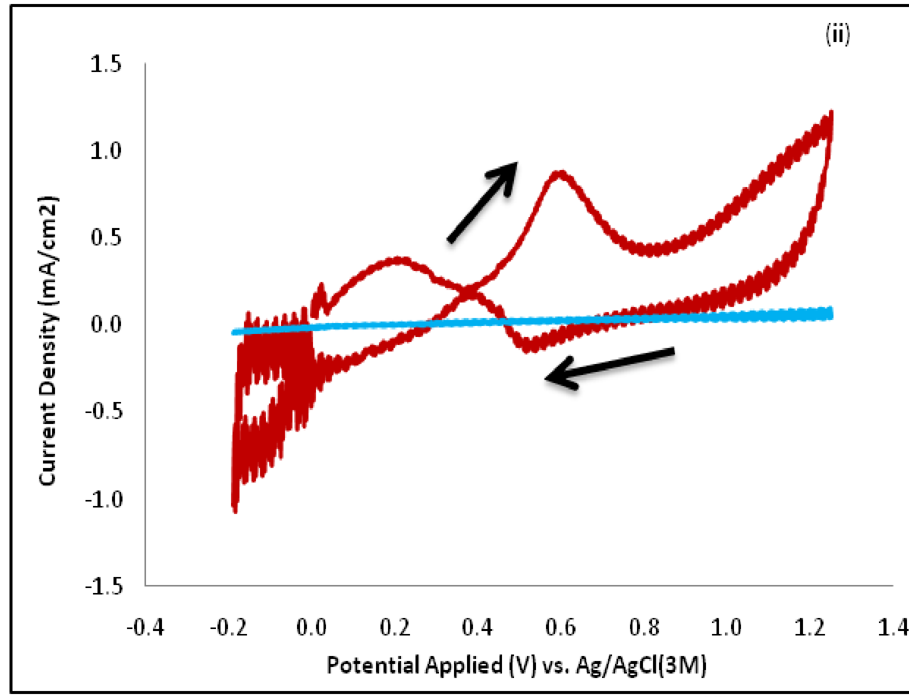
Pt supported on Carbon paper: Electrochemical Evaluation

Cyclic voltammograms at 50 mV/s

(i) 0.1 M HClO4 + CO saturated



(ii) 0.1 M HClO4 + 0.1 M Methanol



Catalyst showed activity towards methanol electro-oxidation in acid media

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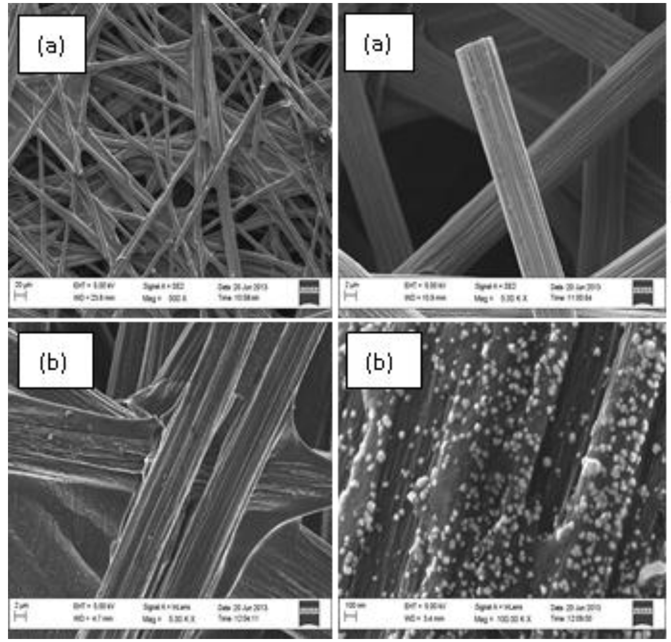
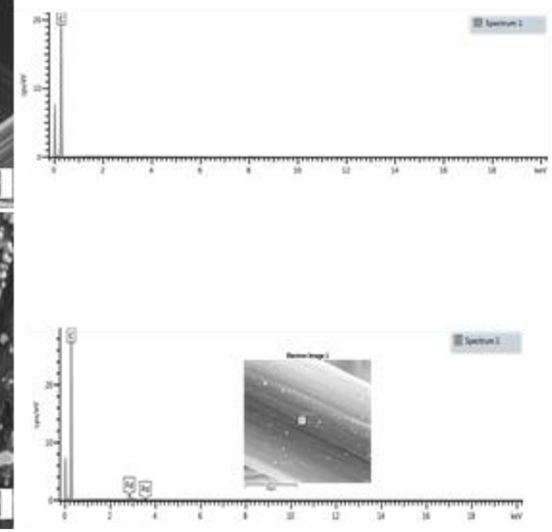
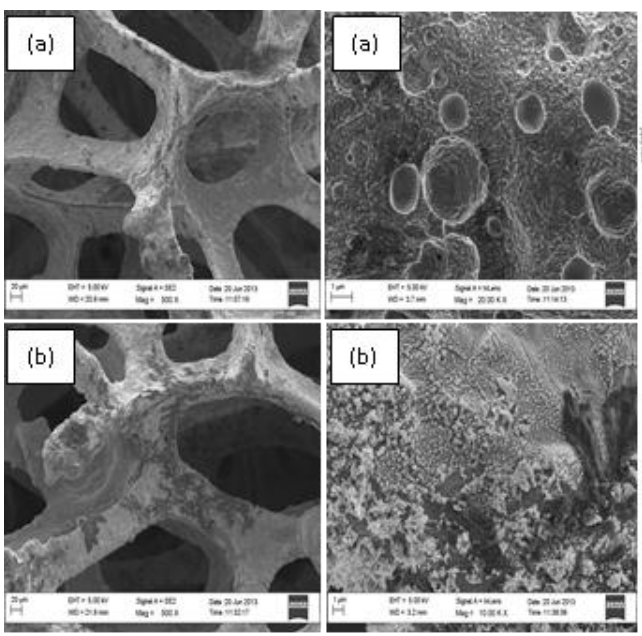
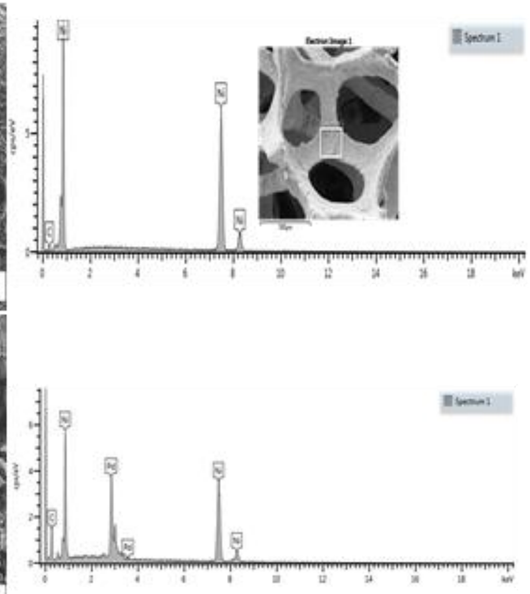
Pd/carbon paper and Ni foam: SEM micrographs and EDX profile

Carbon paper





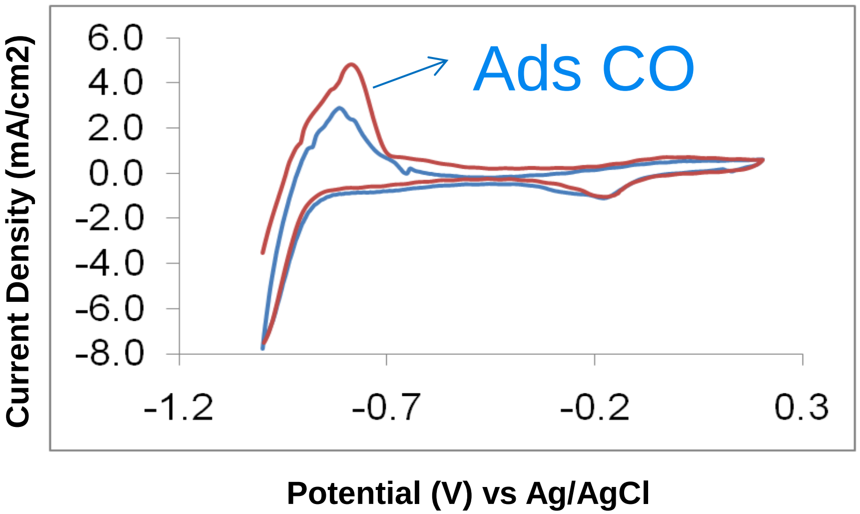




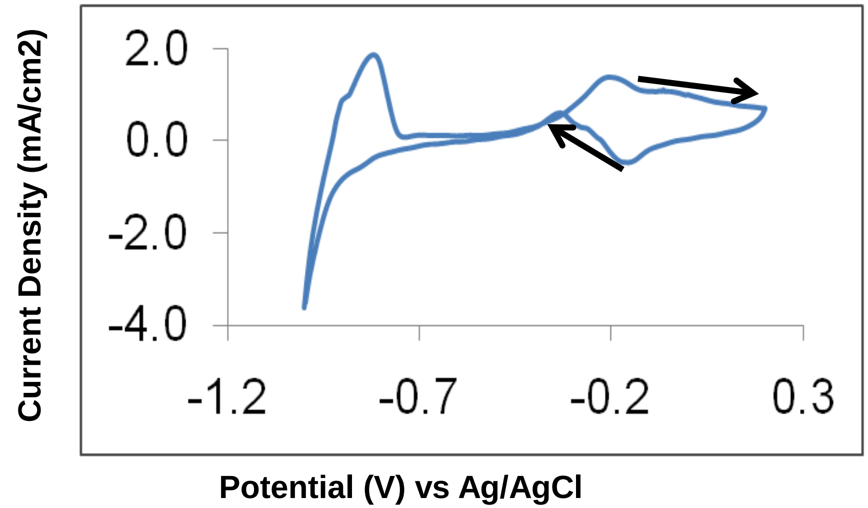
Nickel foam

Pd supported on Carbon paper: Electrochemical Evaluation

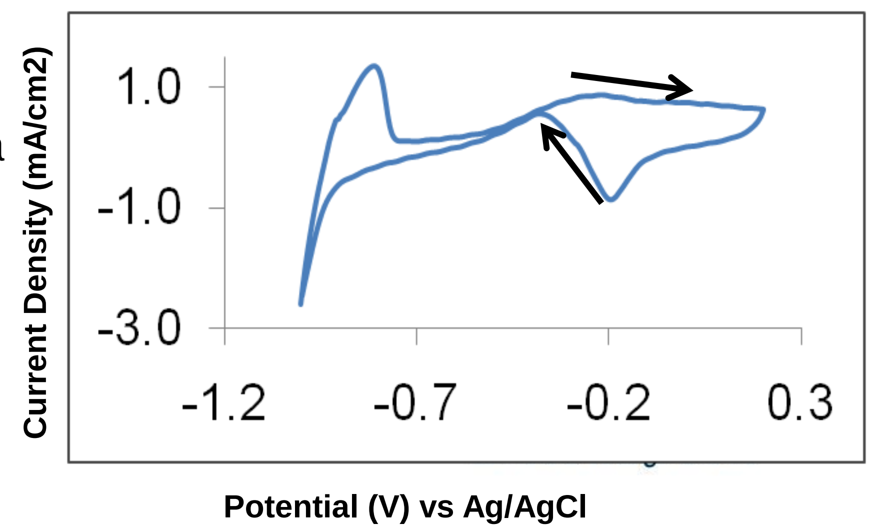
(i) 0.1 M KOH + CO and N2



(ii) 0.1 M KOH + 0.1 M Methanol



(iii) 0.1 M $HClO_4$ + 0.1 M Ethanol



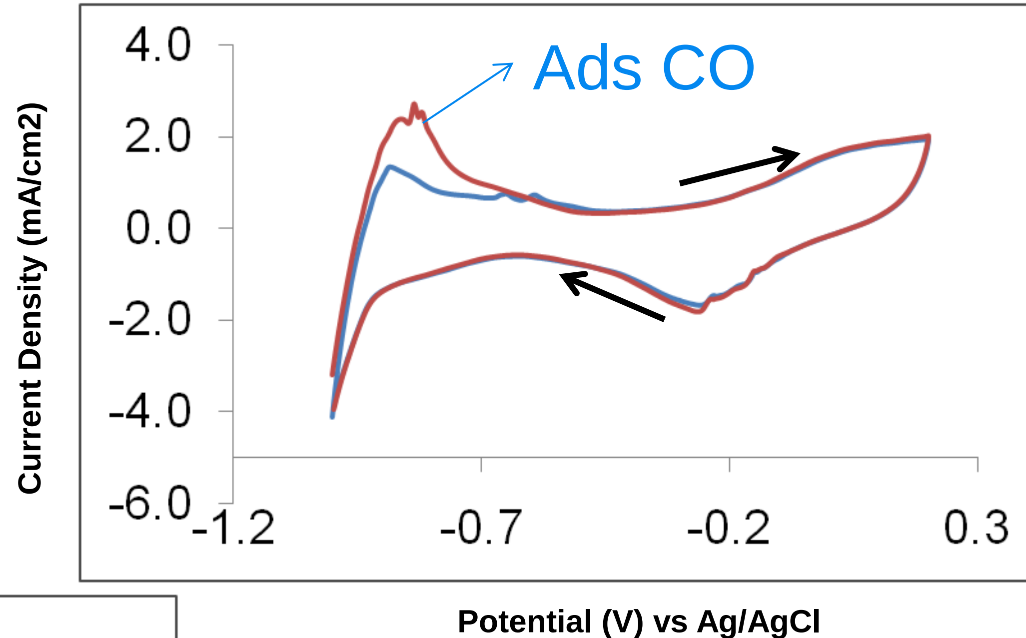
Catalyst showed activity towards methanol and ethanol electrooxidation in alkaline media

Catalyst is tolerant to CO poisoning

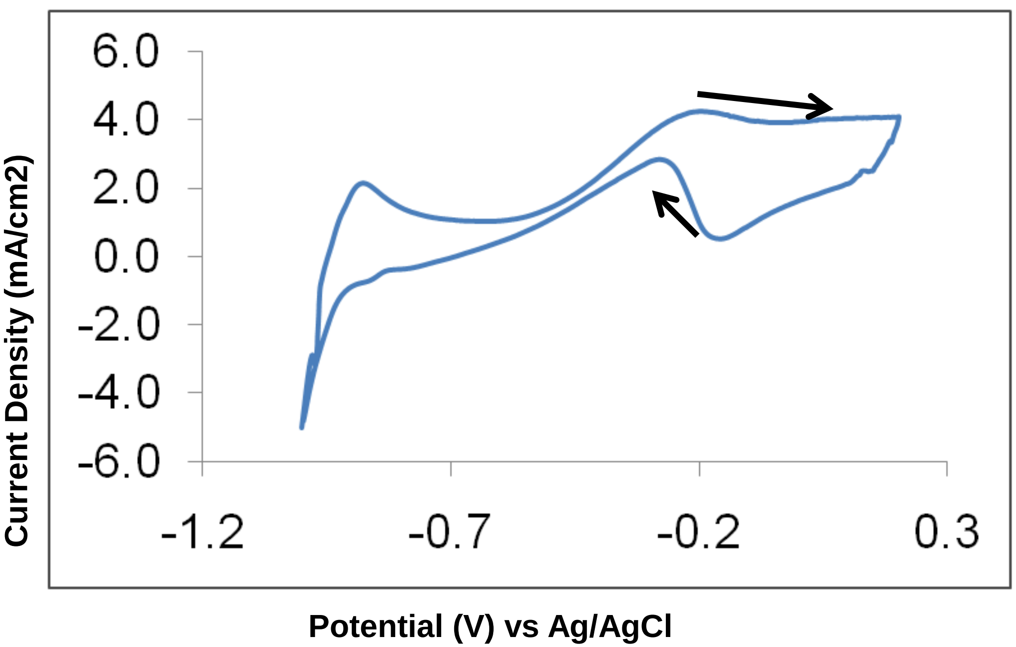
Pd supported on Ni foam: Electrochemical Evaluation

Catalyst	Methanol Onset potential (V) vs Ag/AgCl	Ethanol Onset potential (V) vs Ag/AgCl
Pd/C paper	-0.456	-0.555
Pd/Ni foam	-0.429	-0.590

(i) 0.1 M KOH + CO and N2



(ii) 0.1 M KOH + 0.1 M Ethanol



MeOH: 27 mV more negative on Pd/Carbon paper

EtOH: 35 mV more negative on Pd/Ni foam

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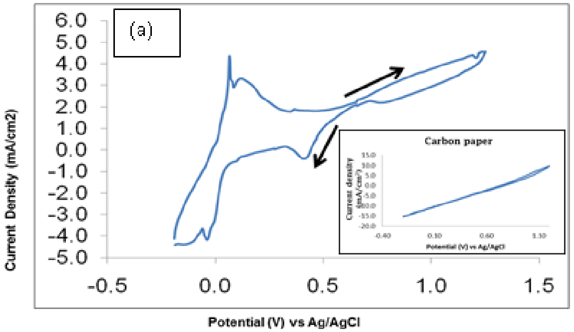
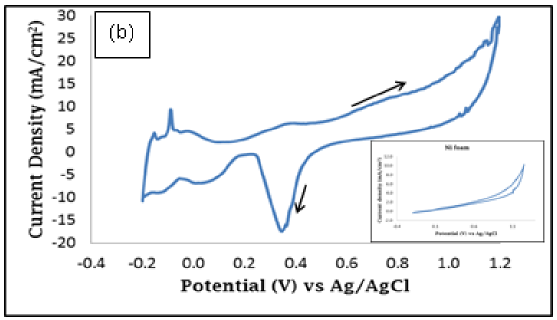
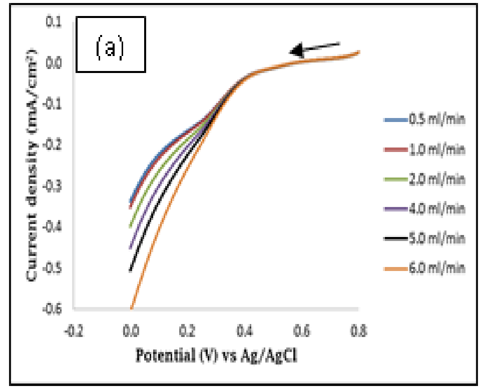
Pd on Carbon paper or Ni foam: Electrochemical Evaluation- ORR

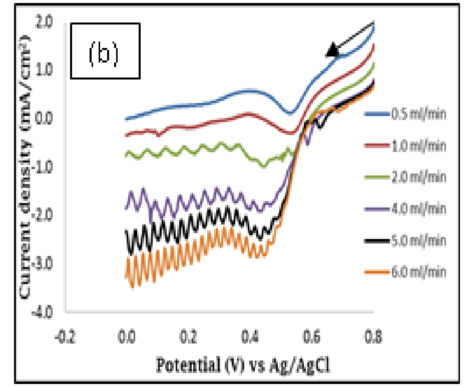
(i) CV in 0.1 M $HClO_4$ + N_2 at 50 mV/s

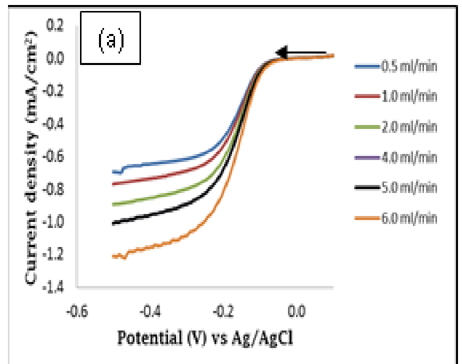


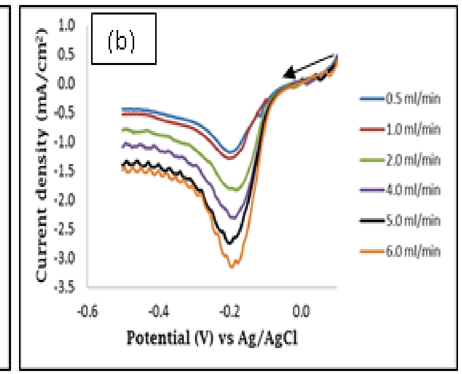


(ii) LSV in 0.1 M HClO4 + O_2 at 10 mV/s
(iv) LSV in 0.1 M KOH + O_2 at 10 mV/s

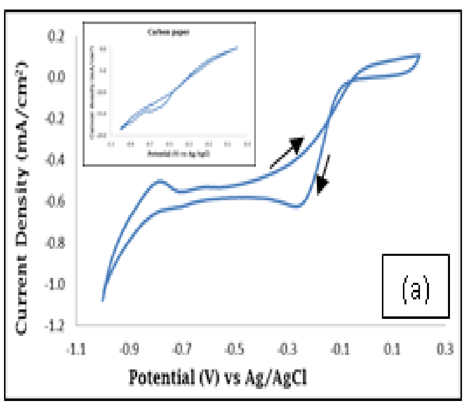


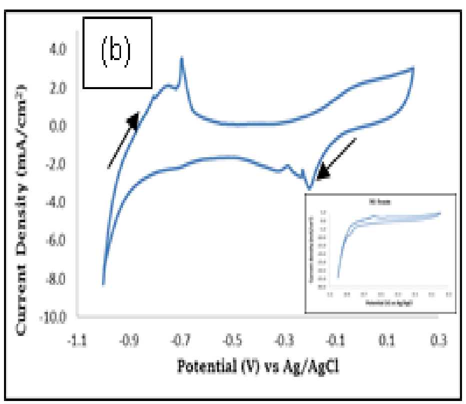


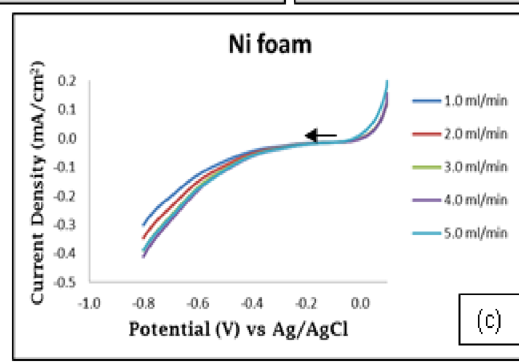




(iii) CV in 0.1 M KOH + N_2 at 50 mV/s







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Electrochemical evaluation: summary

at 3 ml/min, 10 mV/s

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

Acid: 200 mV more positive on Pd/Ni foam than on Pd/Carbon paper

Alkaline: 21 mV more positive on Pd/Ni foam Pd/Carbon paper
: 456 mV more positive on Pd/Ni foam than on Ni foam
Ni foam is a better substrate than carbon paper
Pd enhanced the activity on Ni foam

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Future Work

- Membrane work: FC testing including AE ionomer optimisation
- Electrocatalysis: MEA fabrication and FC testing under active conditions
- FC tests using MEAs fabricated with ECALD technique
- Intense FC tests in collaboration with, for example, HySA, Korea, Argentina

- Ultimately, proudly South African materials for local and export markets

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