

***Carbon supported Pd-Ni and Pd-Ru-Ni
nanocatalysts for the alkaline direct ethanol
fuel cell (DEFC)***

ASME2011, Washington, DC

Mkhulu K Mathe

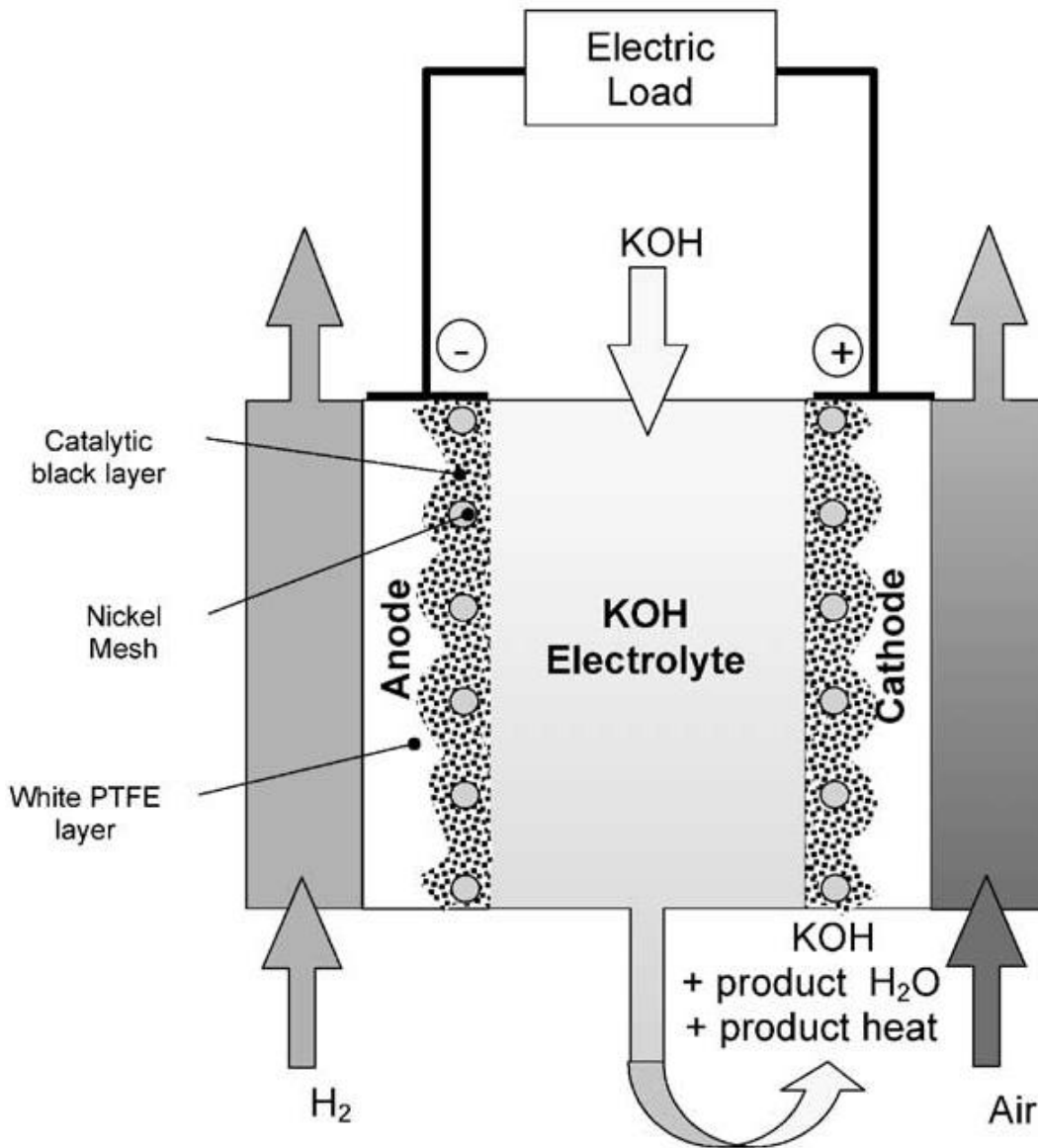


Outline

- Background and Introduction
- Synthesis of Electrocatalysts
- Characterization and Evaluation of the Electrocatalysts
- Performance measurement of the Electrocatalysts
- Concluding remarks
- Acknowledgements

- **DEFC anode studies**

- synthesis
- Electrooxidation
- Performance

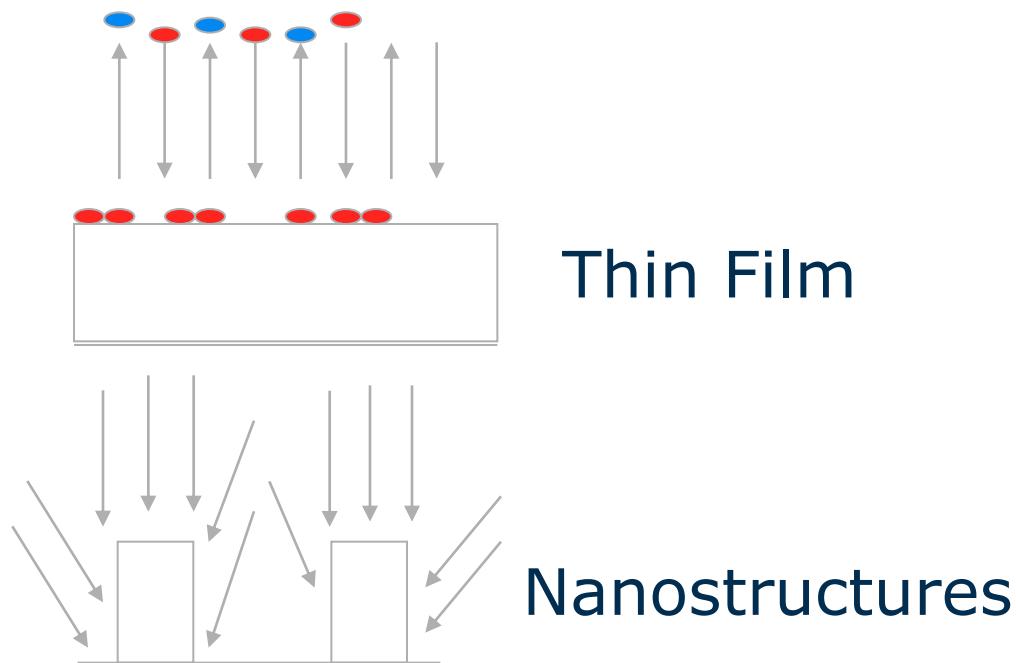


Synthesis of electrocatalysts

catalytic active sites (active reaction area)

surface-to-volume ratio

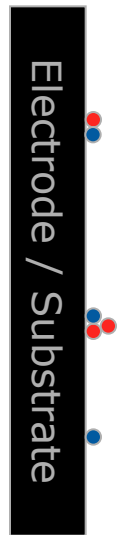
transport of reactants and products



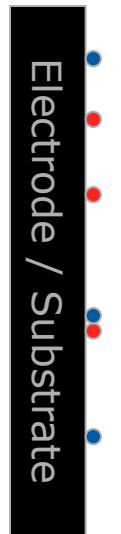
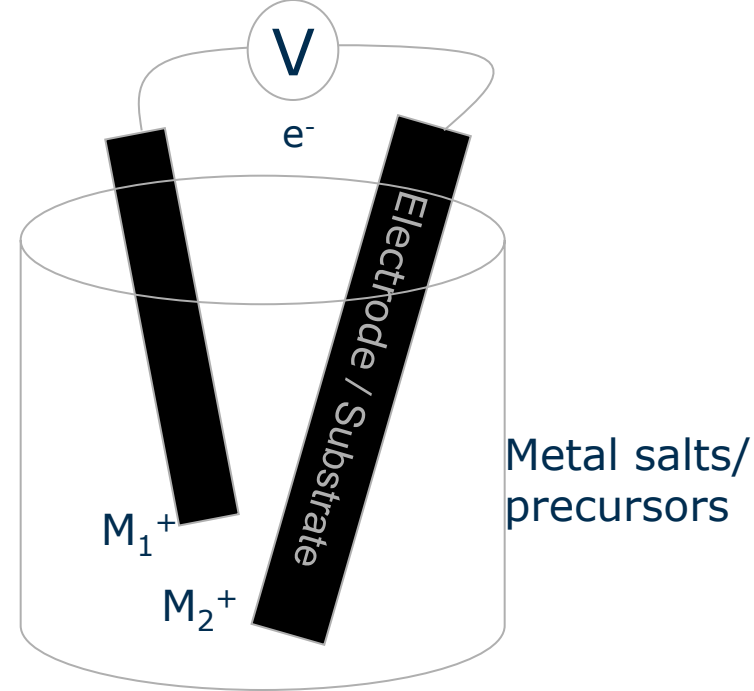
CSIR

Electrocatalyst particles have to maintain electronic contact with support

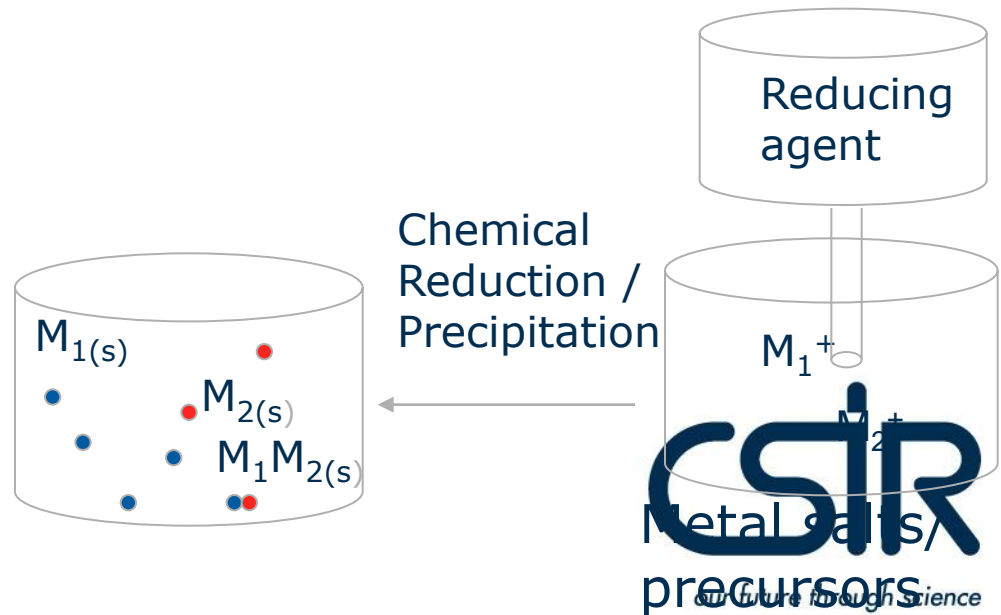
Chemical routes to Nanoparticulate Multimetallic Electrocatalysts



Electrochemical deposition
 e^-



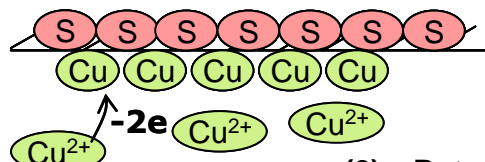
Transfer
To Electrode



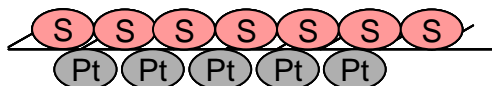
Sequential deposition coupled to Surface-limited Redox-replacement reactions (SLRR): Synthesis of multilayered bimetallic RuPt electrocatalyst



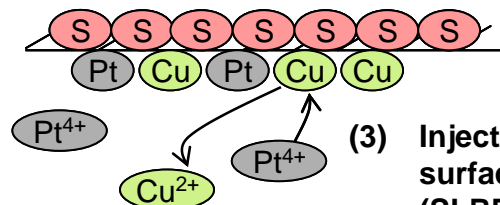
(1) Clean substrate with blank electrolyte (BE);
Inject Cu^{2+} solution at $E \gg E_{\text{Cu-Cu}^{2+}}$



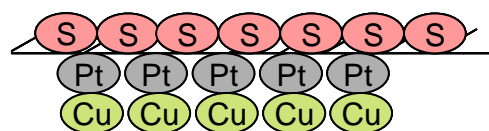
(2) Potentiostatic electrodeposition at $-E_{\text{dep}} > E_{\text{Cu-Cu}^{2+}}$ (Underpotential Deposition (UPD)) or $-E_{\text{dep}} < E_{\text{Cu-Cu}^{2+}}$ (small Overpotential Deposition (OPD)) - to produce sacrificial Cu adlayer on active sites of the substrate; Rinse with BE



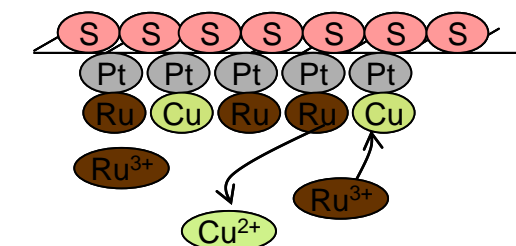
(4) Pt nanodeposit on substrate;
Rinse with BE and inject Cu^{2+} solution at $E \gg E_{\text{Cu-Cu}^{2+}}$



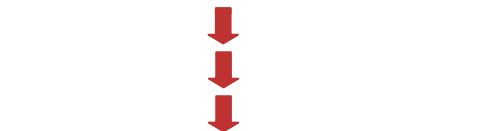
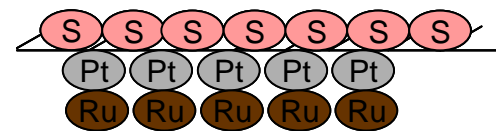
(3) Inject H_2PtCl_6 solution and allow surface-limited redox-replacement (SLRR) of Cu by Pt at open circuit (OC)



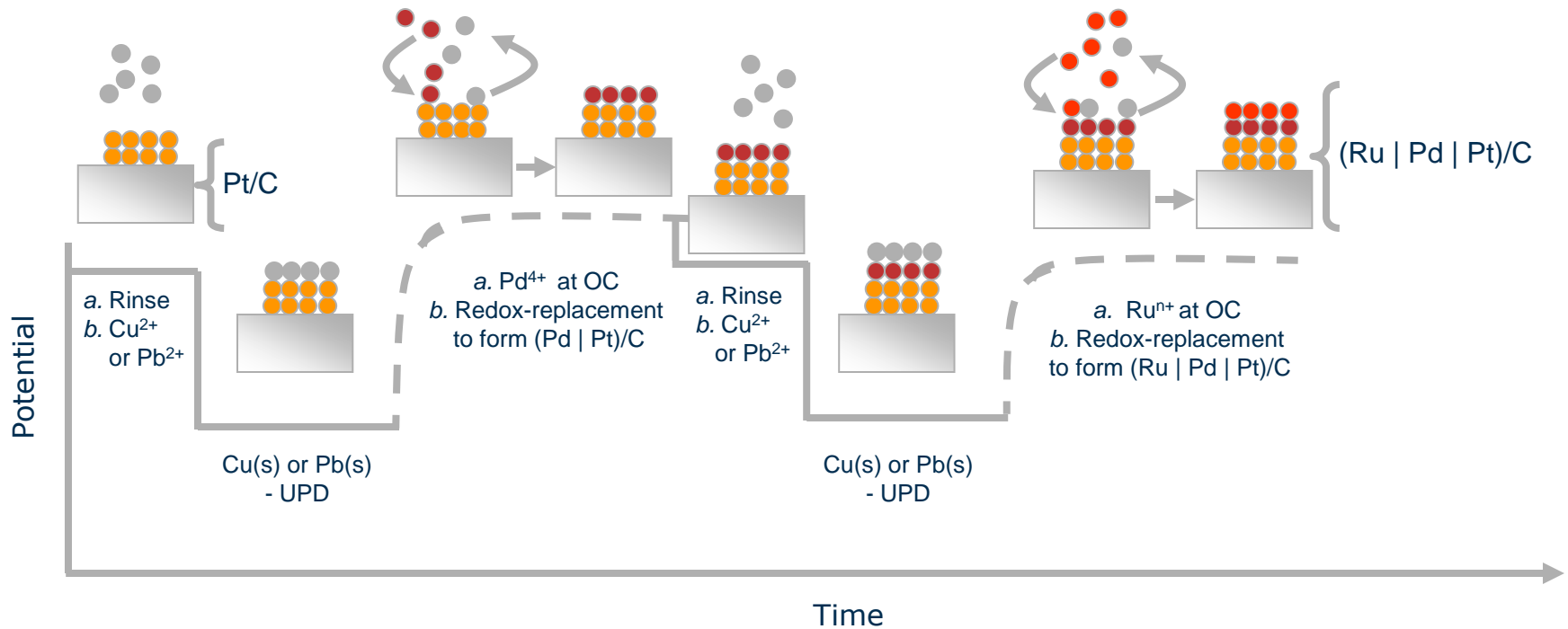
(5) Potentiostatic electrodeposition at $-E_{\text{dep}}$ to produce sacrificial Cu adlayer on active sites on Pt adlayers; Rinse with BE



(6) Inject RuCl_3 solution and allow surface-limited redox-replacement (SLRR) of Cu by Ru at OC



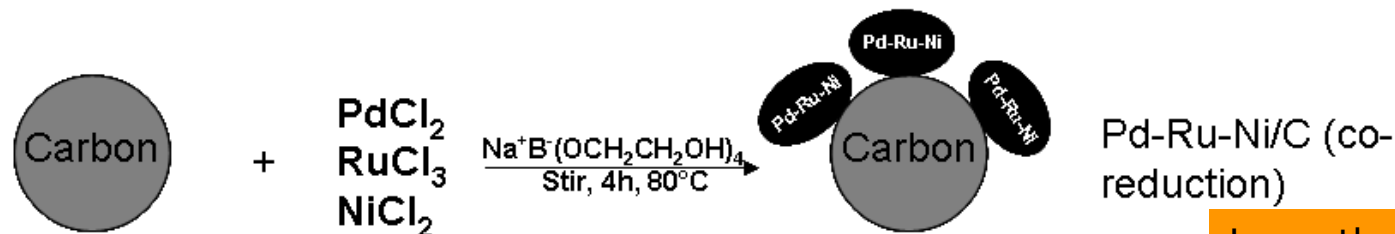
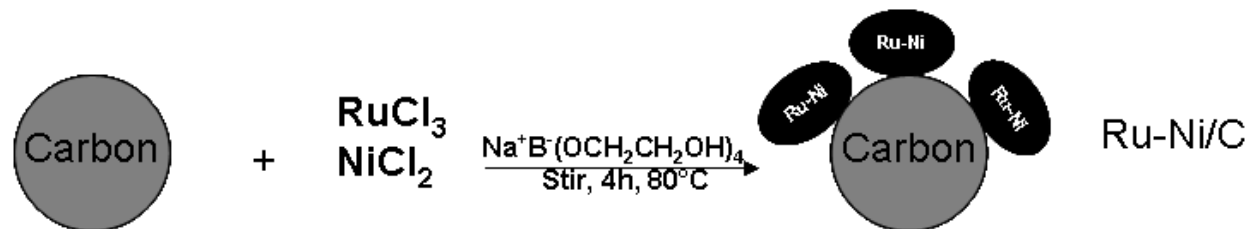
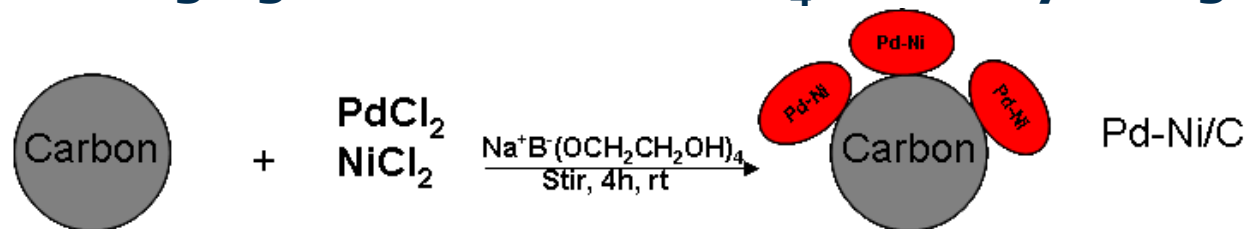
Multi-stage electrodeposition



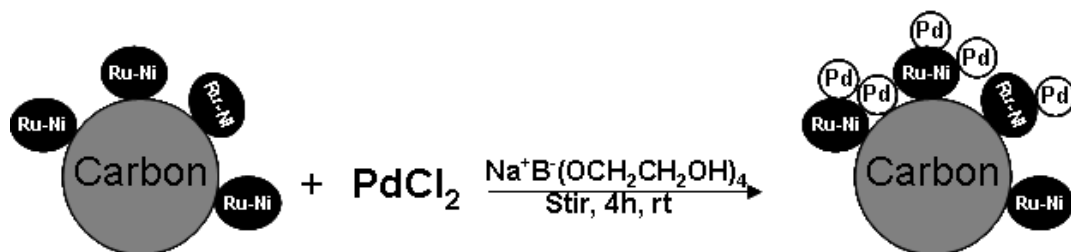
Noble-Metals studied = Pt, Ru, Au, Pd
Substrates = Carbon materials, Gold films

Synthesis of Electrocatalysts

reducing agent: mixture NaBH_4 and ethylene glycol

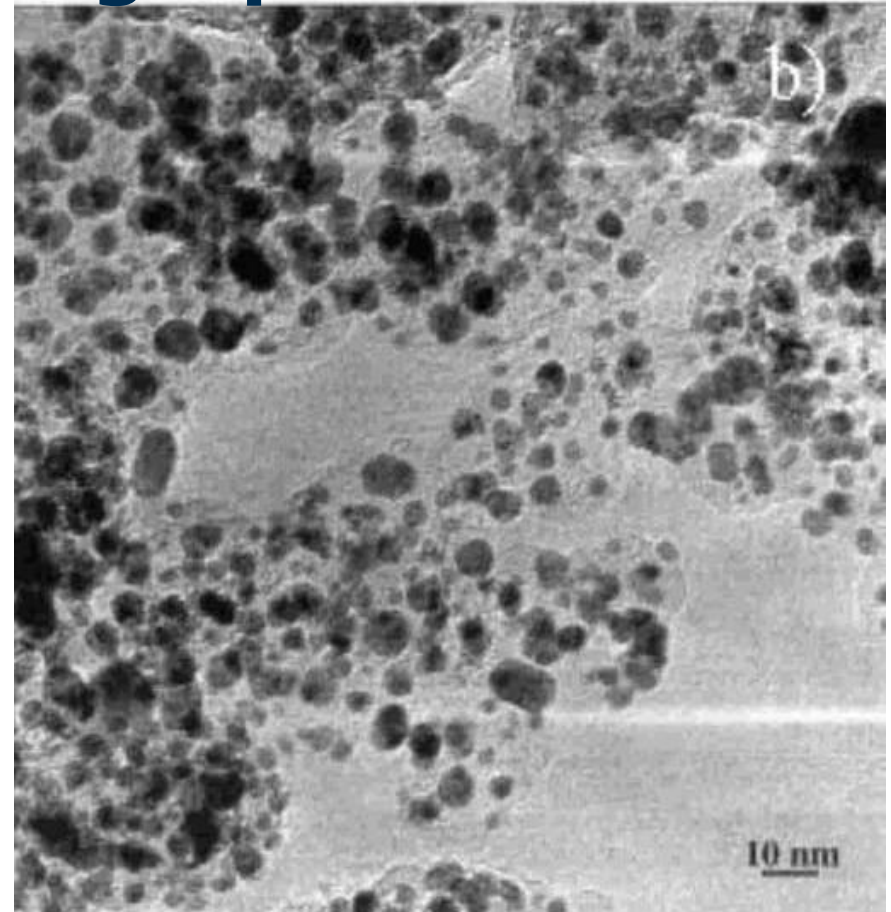
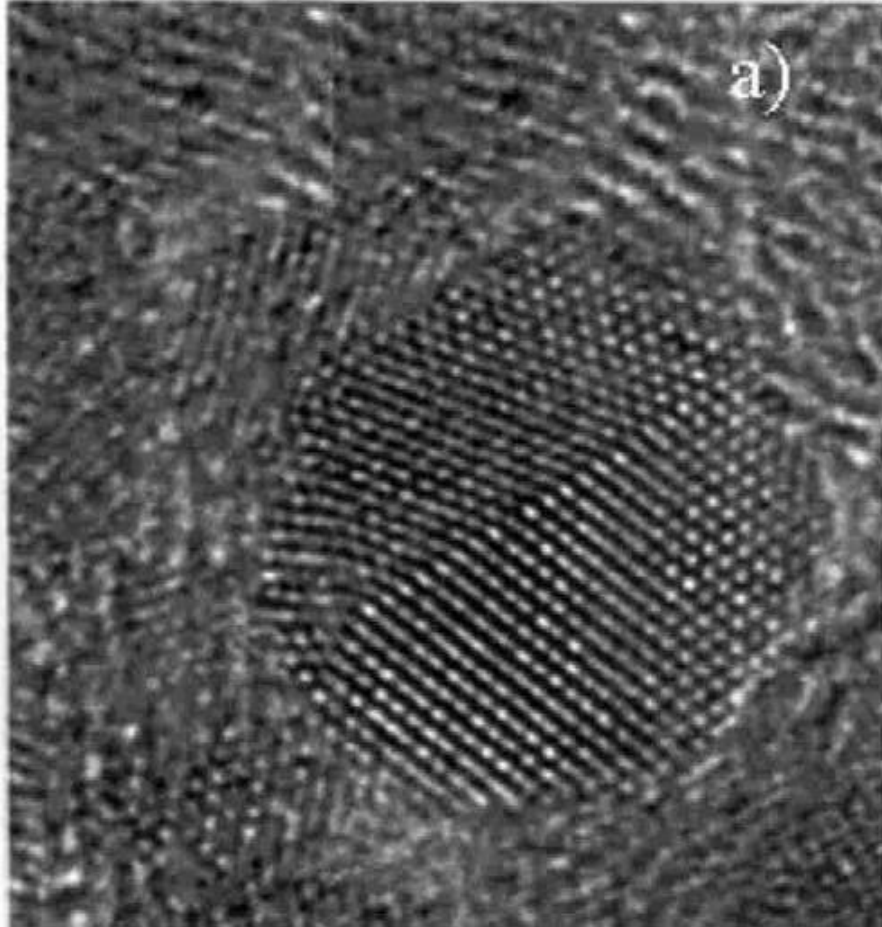


Low ethanol oxidation performance vs Pd+Ru-Ni/C



Pd + Ru-Ni/C

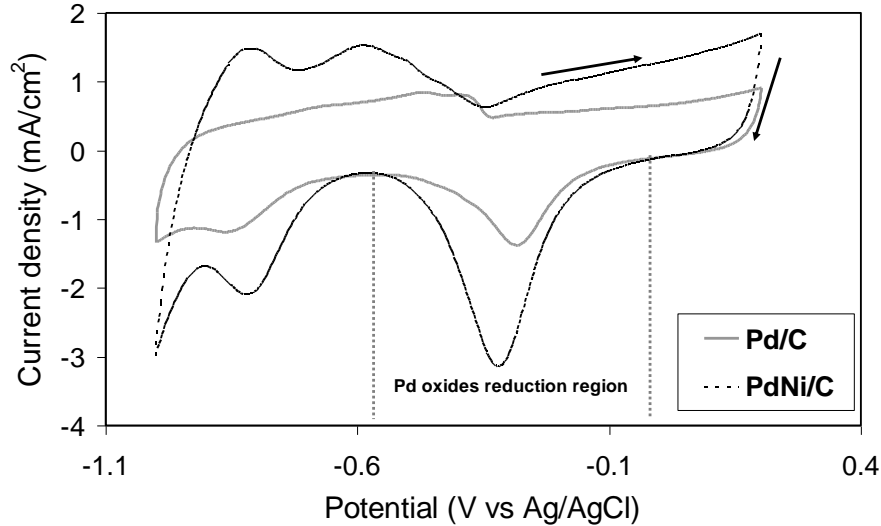
HRTEM and TEM micrographs



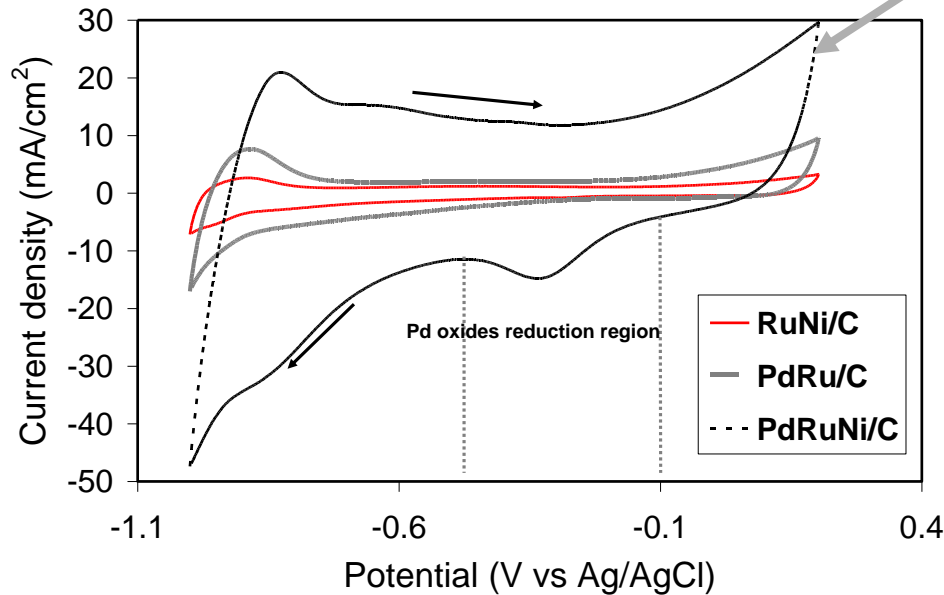
- (a) a twinned single Pt₂Ru₃ nanoparticle of ca. 4.39/0.3 nm characteristic dimensions.
(b) distribution of Pt₂Ru₃ bimetallic nanoparticles on the high-surface area carbon support.

Electrochemical characterization

cyclic voltammograms in 0.5 M NaOH



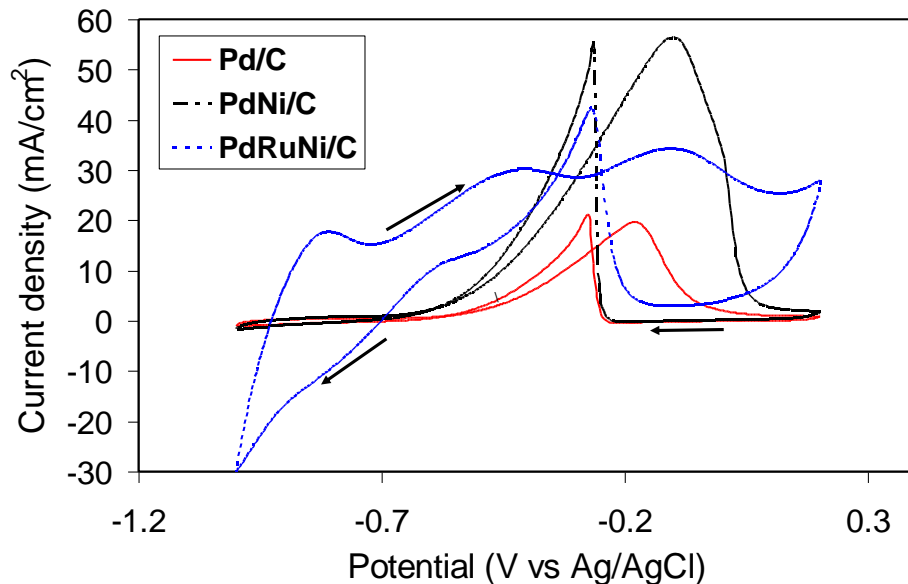
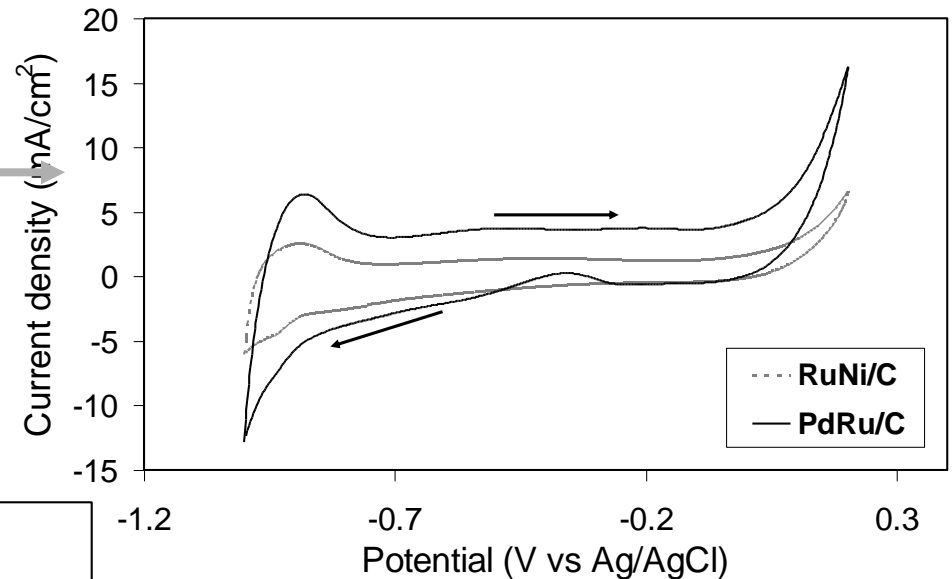
Pd+ Ru-Ni/C



Electrochemical characterization

cyclic voltammograms in ethanol

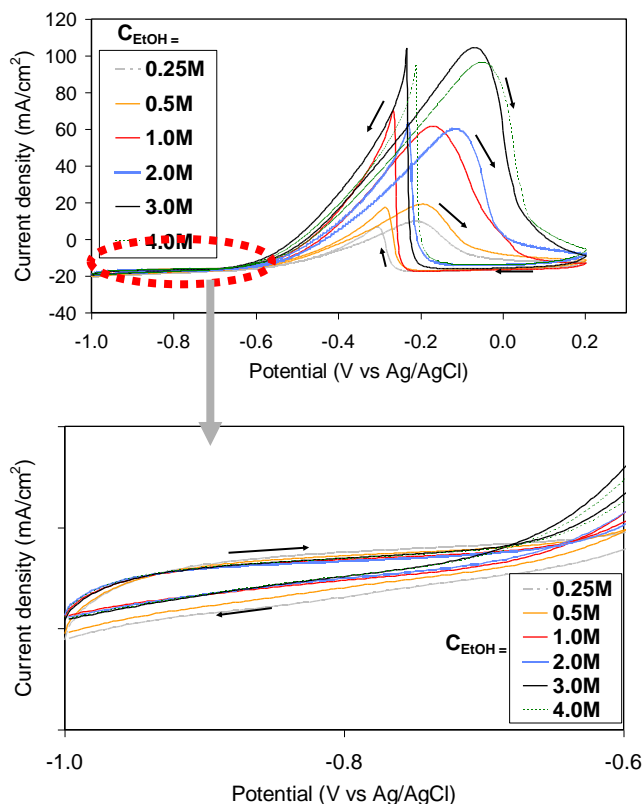
RuNi/C and PdRu/C:
no or low activity towards
ethanol oxidation



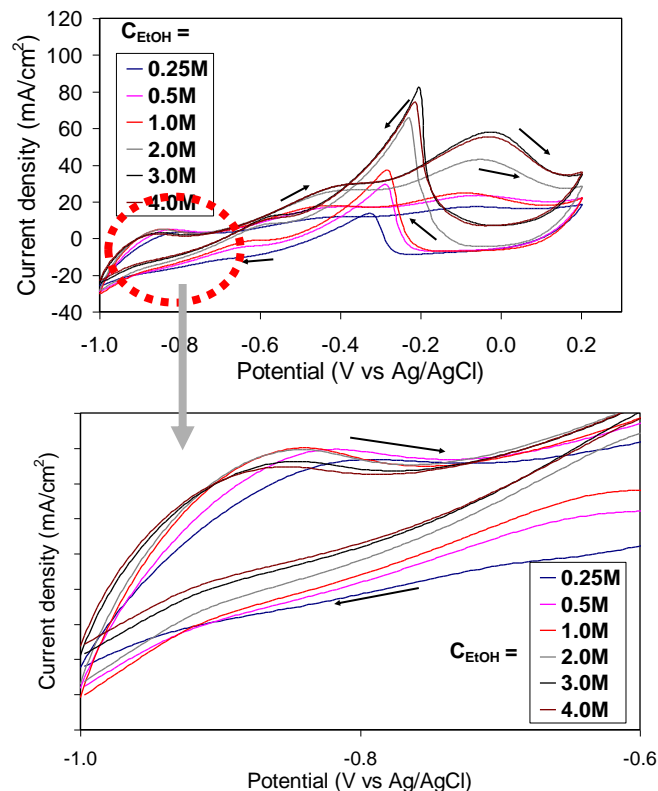
Concentration studies effect on current density

Effect of ethanol concentration

PdNi/C



PdRuNi/C

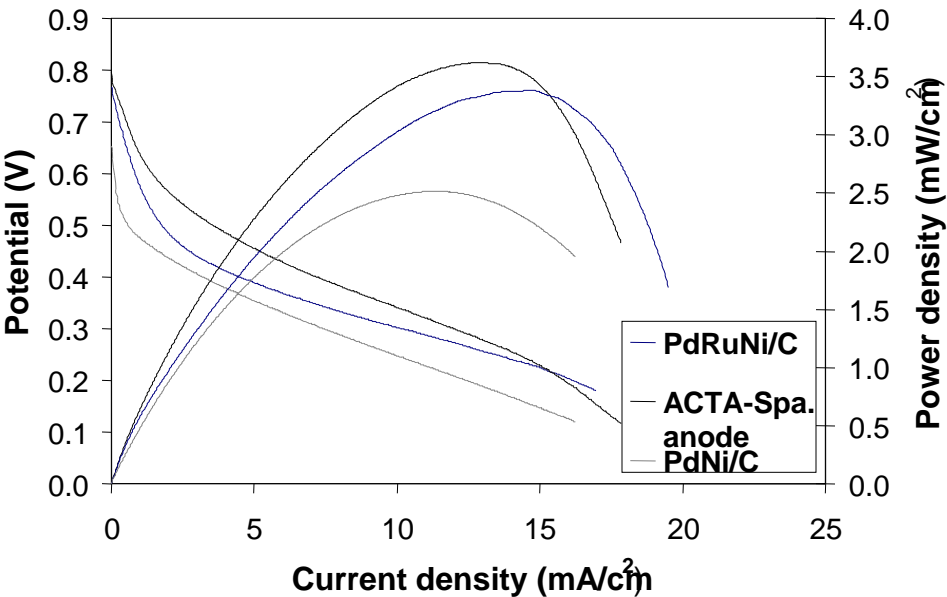


Raising ethanol concentration up to 3 M increased the coverage of the adsorbed ethoxy (CH_3COads) species on the nanocatalyst surface, thus yielding an increase in current density

Electro-catalyst performance: passive alkaline DEFC

cell polarisation and current density curves

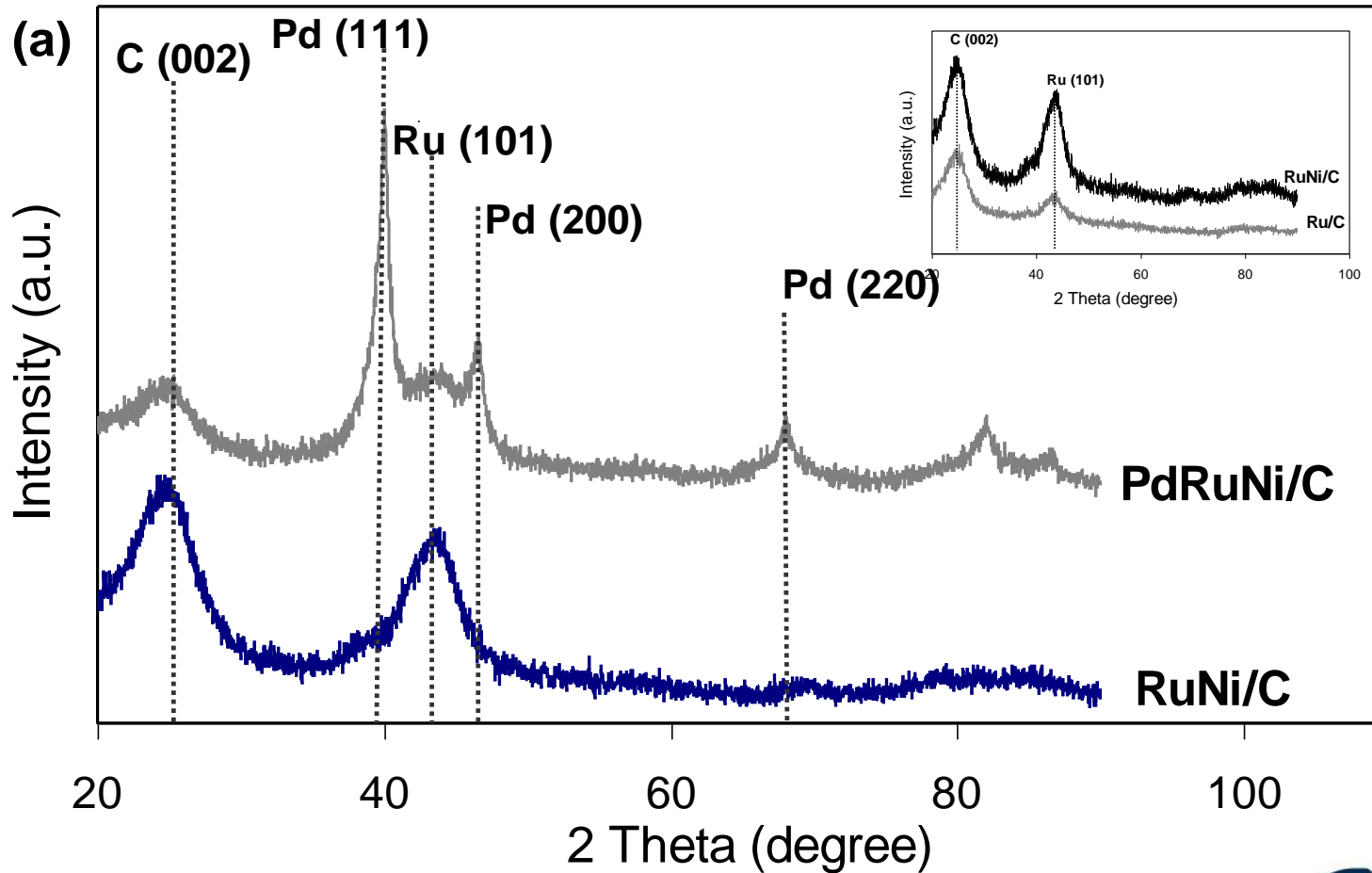
loading vs. ocv



Electro-catalyst	Open circuit voltage (V)	Power/total loading (mW/mgPd)
PdCeO ₂ /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)

XRD micrographs of electrocatalysts



(insert XRD patterns of Ru/C and Ru-Ni/C)

Conclusions

- Pd-Ni/C and Pd-Ru-Ni/C were prepared by chemical reduction method
- nanocatalysts (A&B) higher activities towards ethanol electro-oxidation
- effect of ethanol concentration variation – current density
- binary Pd-Ni/C performs better than ternary nanocatalyst – current density

ACKNOWLEDGEMENTS

- Energy & Processes Team
- CSIR Executive



CSIR

our future through science

Thank You



References

- G.F. McLean et al. International Journal of Hydrogen Energy 27 (2002) 507 – 526
- A.V. Tripkovic´ et al. Electrochimica Acta 47 (2002) 3707/3714
- T.S. Mkwizu, et.al. 219th ECS Meeting, 1 – 6 May, 2011, Montreal, Canada