

Supplementary Information

Improving the electrocatalytic activity of Pd nanoparticles through electronic coupling interaction with a Ni₂P–MoS₂ hybrid support for ethanol electrooxidation in an alkaline medium

Thabo Matthews^{a,b,c,*}, Makhaokane Paulina Chabalala^{b,c}, Siyabonga Patrick Mbokazi^{b,c}, Memory Zikhali^{b,c}, Tarekegn Heliso Dolla^d, Anatolijs Šarakovskis^e, Guntars Vaivars^{e,f,g}, Tunde Lewis Yusuf^h, Rhiyaad Mohamed^a, Nobanathi Wendy Maxakato^{b,c,*}

^aHySA/Catalysis Centre of Competence, Catalysis Institute, Department of Chemical Engineering, University of Cape Town, Cape Town 7701, South Africa

^bDepartment of Chemical Sciences, University of Johannesburg, Doornfontein, 2028, South Africa

^cCenter for Nanomaterials Research, University of Johannesburg, South Africa

^dInstitute for Catalysis and Energy Solutions (ICES), College of Science, Engineering and Technology, University of South Africa (UNISA), Private Bag X6, Florida, 1710, South Africa

^eInstitute of Solid State Physics, University of Latvia, Kengaraga Iela 8, LV-1063 Riga, Latvia

^fFaculty of Chemistry, University of Latvia, Jelgavas Iela 1, LV-1004 Riga, Latvia

^gInstitute of Chemical Physics, University of Latvia, Jelgavas Iela 1, LV-1004 Riga, Latvia

^hDepartment of Chemistry, Faculty of Natural and Agricultural Sciences, University of Pretoria, Private Bag X20, Hatfield 0028, Pretoria, South Africa

*Corresponding author E-mail address: nmaxakato@uj.ac.za, matthewsThabo@gmail.com and matthews.thabo@uct.ac.za

Table S1. Current loss in percentage obtained from durability test employing chronoamperometry and cyclic voltammetry after 10000 s and 500 cycles, respectively.

Electrocatalyst	*Rate of current loss σ ($\%s^{-1}$)	Current loss (%)		Remarks
		CA	CV	
Pd/Ni ₂ P-MoS ₂	1.63 x 10 ⁻³	66.81	11	<ul style="list-style-type: none"> • MoS₂-(Pd)-Ni₂P Synergy enhances the stability and dispersion of Pd nanoparticles and a high density of active sites. • Strong support for metal interaction and combination of electronic, geometric, and synergistic.
Pd/Ni ₂ P	3.06 x 10 ⁻³	76.03	15	<ul style="list-style-type: none"> • Electronic Interactions lead to alterations in the electronic structure of both materials.
Pd/C	3.94 x 10 ⁻³	82.70	21	<ul style="list-style-type: none"> • Compromised Pd NPs on carbon (agglomeration, coalition)
Pd/MoS ₂	0.014	91.53	42	<ul style="list-style-type: none"> • Pd phase transitions leading to loss of active surface area hence reduced active site

* $\sigma(\%s^{-1}) = \frac{100}{I_0} \left(\frac{dI}{dt} \right)_{t > 2500s}$, long term poisoning rate. We propose that the calculation of $\sigma(\%s^{-1})$ for chronoamperometry is a better way of data evaluation as this equation can be used in the predetermination of stability. The reason is that the calculation involves the rate of change in the current decay trajectory with time. Hence, it is more suited and can be used in place of the I_f/I_b ratio.

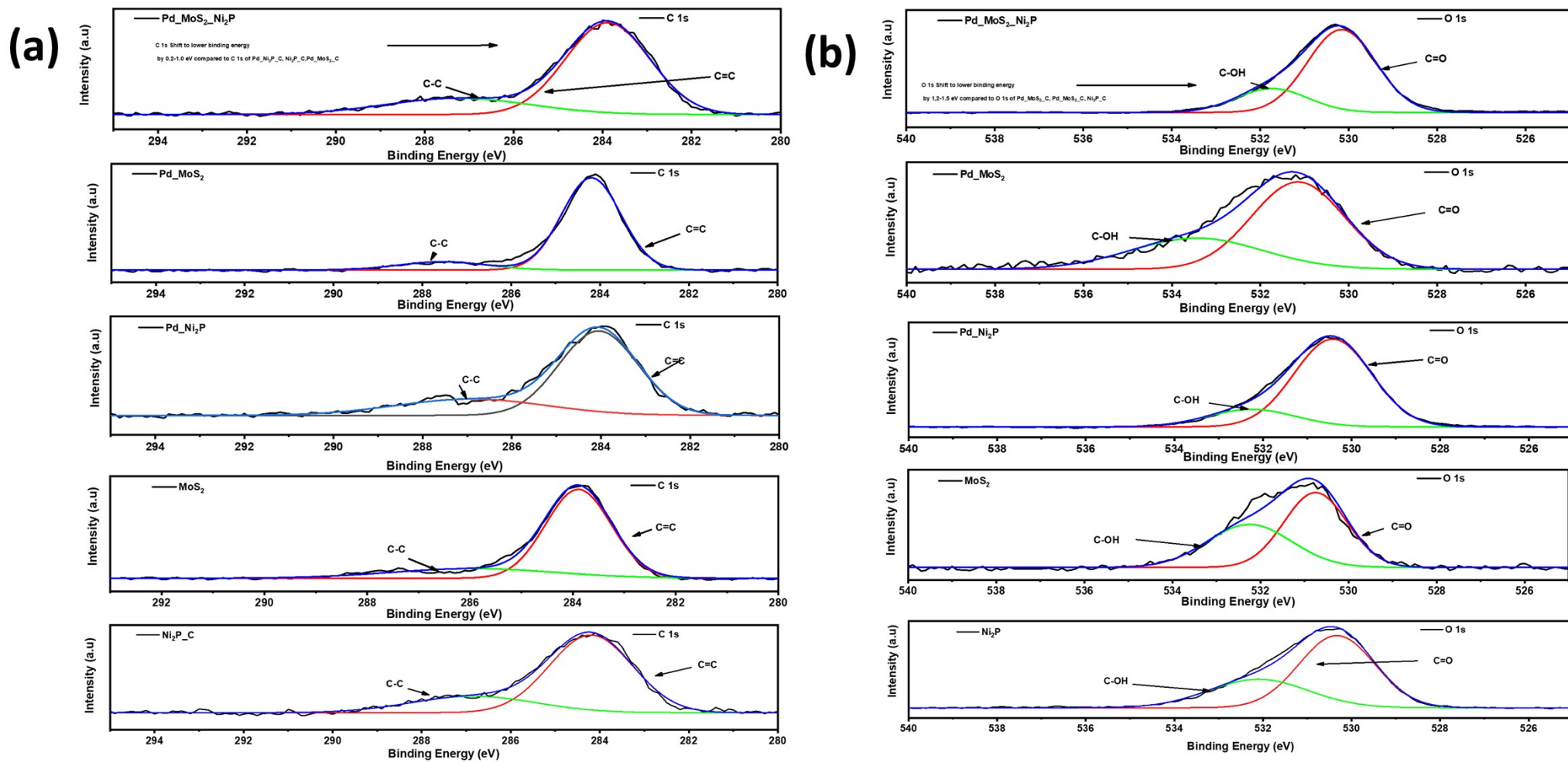


Figure S1: XPS spectra for C 1s and O 1s.

Table S2: Comparison of the mass activity of the prepared electrocatalysts with those reported in the literature for ethanol electrooxidation.

Electrocatalyst	Electrolyte	Current density (i_f)	Scan rate ($\text{mV}\cdot\text{s}^{-1}$)	Reference
Pd/Ni₂P-MoS₂	0.5 M Ethanol + 1 M KOH	1579 mA $\text{mg}^{-1}_{\text{Pd}}$	50	This work
Pd/Ni₂P	0.5 M Ethanol + 1 M KOH	314.8 mA $\text{mg}^{-1}_{\text{Pd}}$	50	This work
Pd/MoS₂	0.5 M Ethanol + 1 M KOH	69.2 mA $\text{mg}^{-1}_{\text{Pd}}$	50	This work
Pd-NiO (6:1 by weight)/C	1 M Ethanol + 1 M KOH	95 mA cm^{-2}	50	[1]
Pd ₂ Ru/C	1.0 M NaOH + 1.0 M ethanol	23 mA cm^{-2}	50	[2]
10%Pd-10%Ag/C	1 M Ethanol + 1 M KOH	~3.7 mA cm^{-2}	50	[3]
Pd/C	Ethanol + 1 M NaOH	~16 mA cm^{-2}	50	[4]

References

- [1] C. Xu, P. kang Shen, Y. Liu, J Power Sources 164 (2007) 527–531.
- [2] J. Guo, R. Chen, F.-C. Zhu, S.-G. Sun, H.M. Villullas, Appl Catal B 224 (2018) 602–611.
- [3] S.T. Nguyen, H.M. Law, H.T. Nguyen, N. Kristian, S. Wang, S.H. Chan, X. Wang, Appl Catal B 91 (2009) 507–515.
- [4] G. Cui, S. Song, P.K. Shen, A. Kowal, C. Bianchini, The Journal of Physical Chemistry C 113 (2009) 15639–15642.