Electronic Supporting Information

A Tetranuclear Cobalt (II) phosphate Possessing a D4R Core: An Efficient Water Oxidation Catalyst

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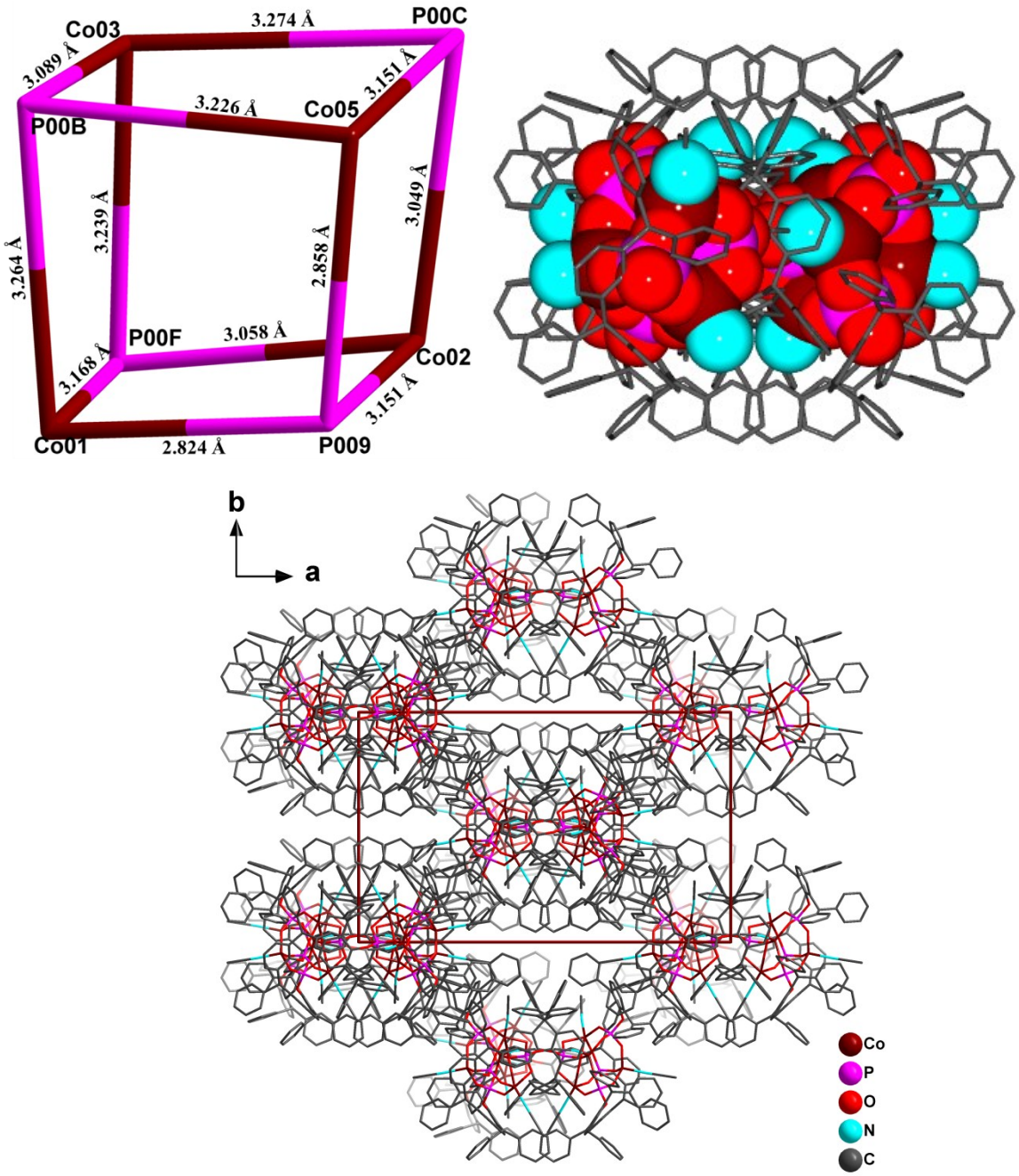


Figure S1: Co_4P_4 distorted cubane core along with edge distances (top left); hydrophobic organic sheath surround the D4R core (top right); line-draw packing along c-axis (bottom) for complex **1**.

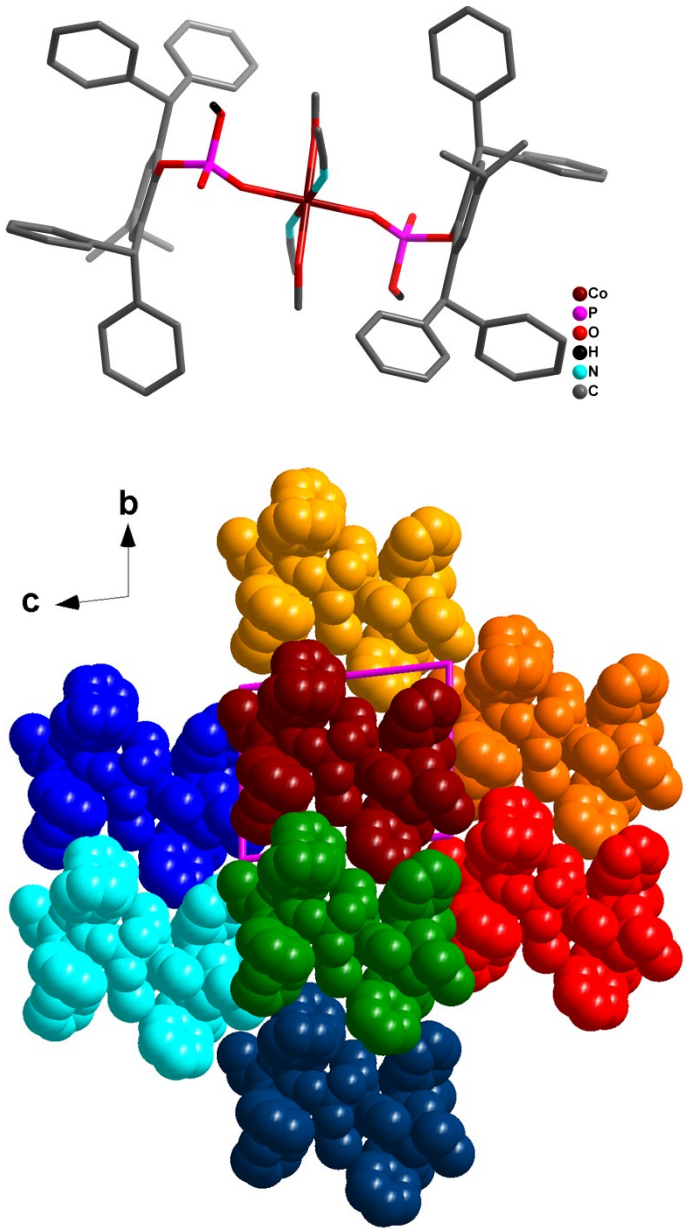


Figure S2: Molecular structure of complex 2 (top); space filling packing diagram (bottom) for complex **2**.

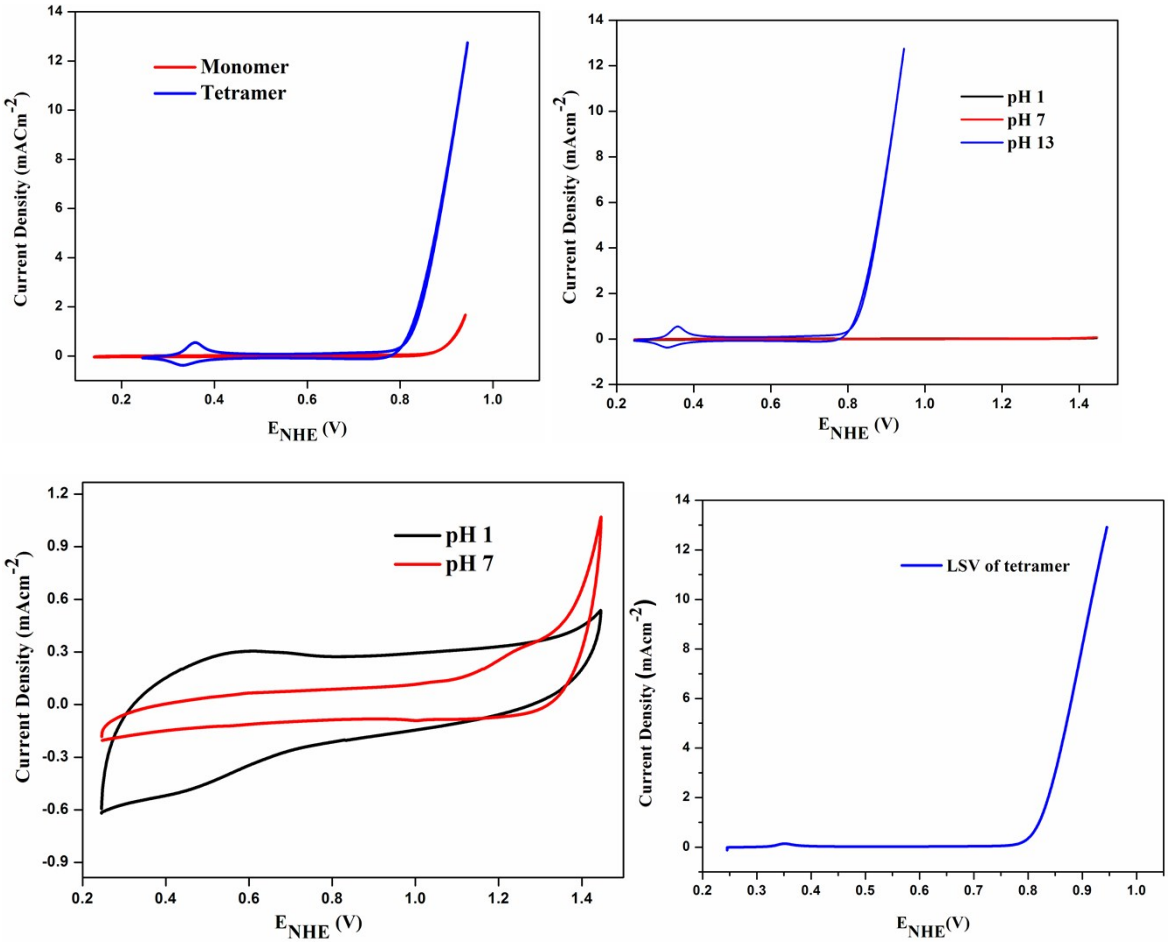


Figure S3: Cyclic voltammograms for complexes **1** (tetramer) and **2** (monomer) (top left); comparison of cyclic voltammograms for complex **1** at different pH (top right); cyclic voltammograms for complex **1** at pH 1 and 7 (bottom left); LSV plot for complex **1** at pH 13.

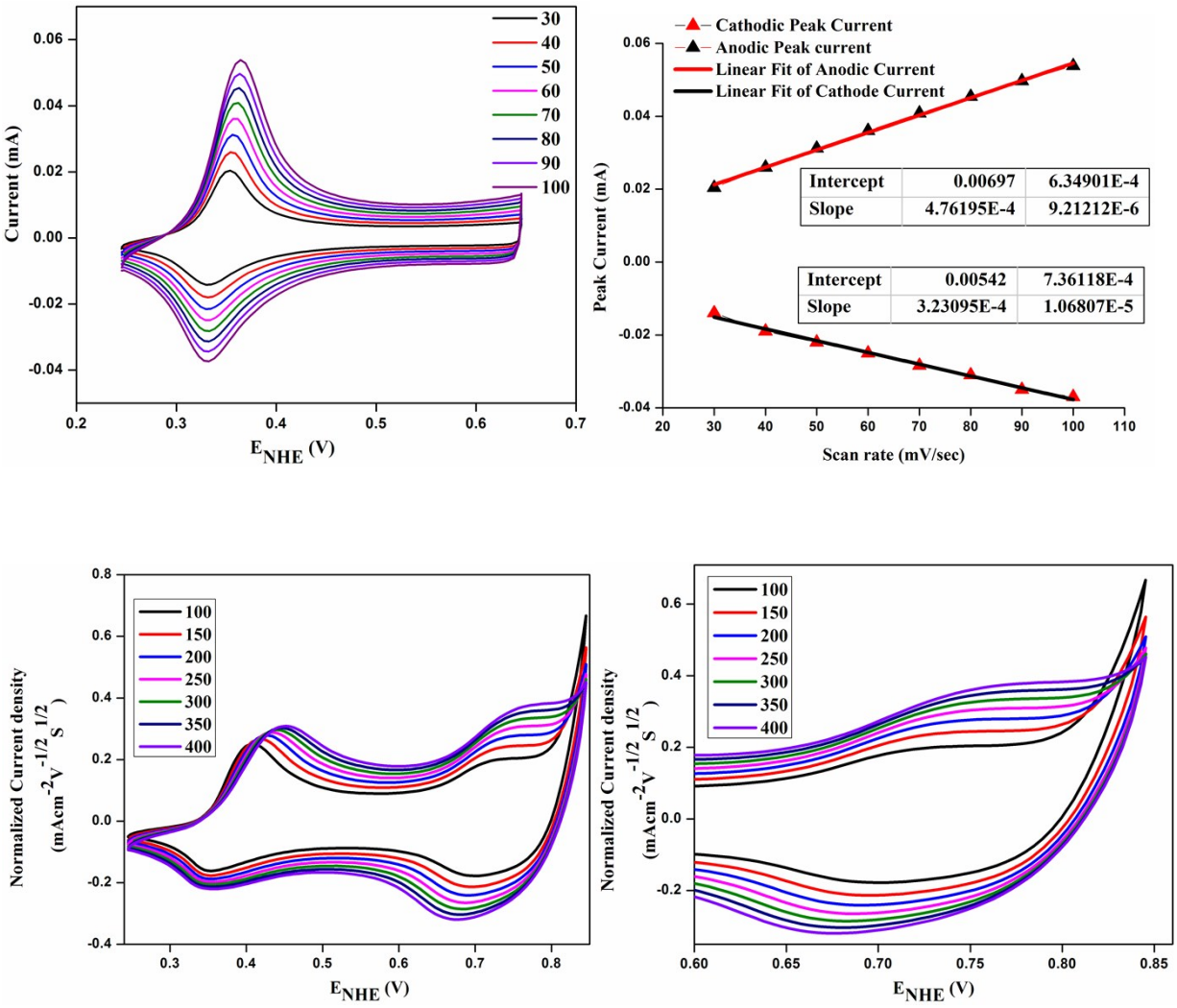


Figure S4: Plot of peak current (corresponds to Co^{II} to Co^{III}) against applied potential (NHE) as a function of scan rate (top left); linear fit of the peak current against scan rates (corresponds to Co^{II} to Co^{III}) for complex **1** at pH 13 (top right); plot of normalized current density at different scan rates (bottom left); decrease of the normalized current density with increasing scan rate (bottom right).

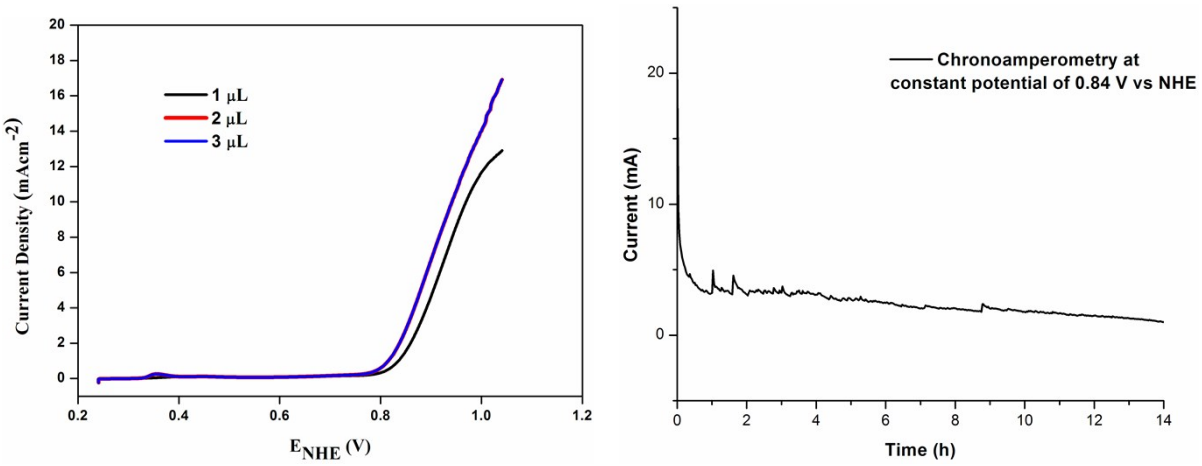


Figure S5: Effect of sample loading on the curent density (left), chronoamperometry experiment at 0.85 V (NHE) for 14 h at pH 13 (right).

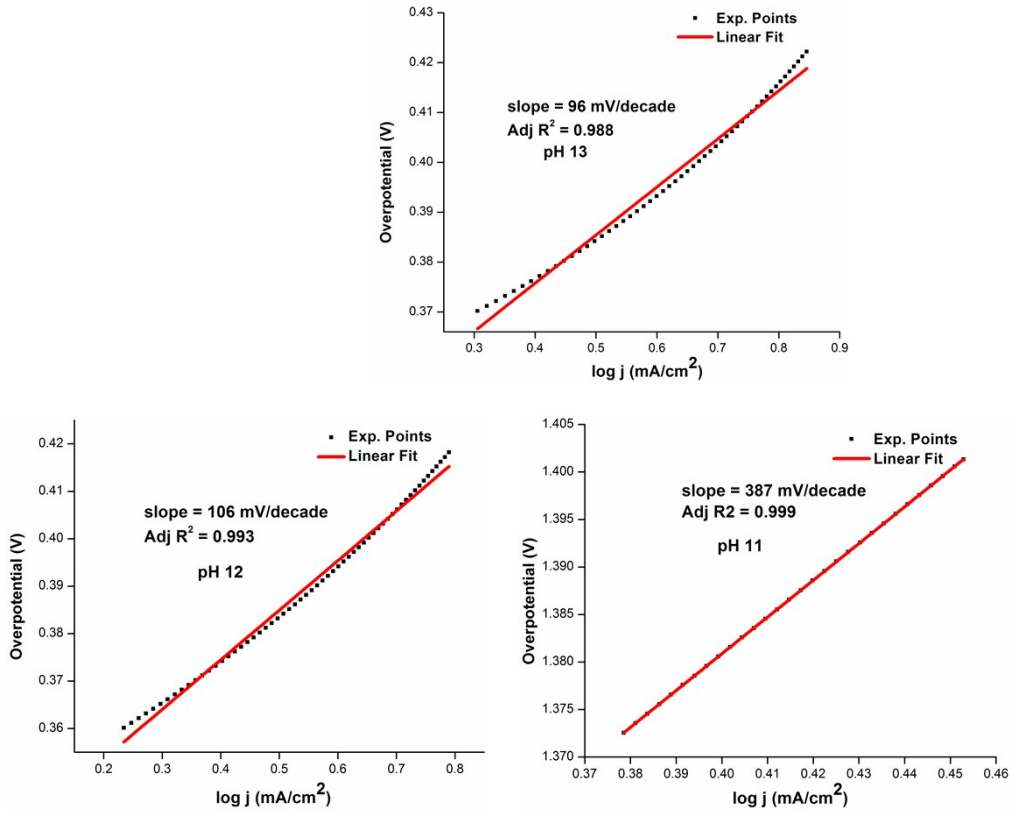


Figure S6: Tafel plots at various pH, the value of Tafel slope increases with decreasing pH from 13.

Turn over frequency (TOF) calculation

This parameter estimates the surface concentration of active cobalt species on the modified glassy carbon electrode. From the oxidation peak of cobalt, one can measure the TOF parameter according to the reported method [J. Am. Chem. Soc. 2013, 135, 13270−13273]. Initially before going to start oxygen evolution reaction, cobalt based monomer shows a clear oxidation peak in between 0.36 V (vs NHE) which corresponds to the Co^{2+} to Co^{3+} conversion. A linear relation between the scant rate and oxidation peak current provides us a slope which is incorporated in the equation (1) to find out the total active centers ($A\Gamma_0$) for the OER. From OER current at a particular overpotential, one can calculate turn over frequency using equation 2.

$$\Gamma_0 = \frac{4RT}{An^2F^2}(slope) \quad ...(1)$$

$$TOF = \frac{Current\ at\ \eta}{4F\ (\Gamma_0)} \quad ...(2)$$

where A = Electrode surface area (here geometrical surface is considered); R= universal gas constant; T = Temperature; n = 1, no. of electron transfer during Co^{2+} to Co^{3+} formation; F = Faraday constant; η = overpotential; Γ_0 = number of active Co atoms/cm^2.

With slope 4.76×10^{-4} (Anodic peak current), Γ_0 (number of active Co atoms/cm^2) is calculated as 7.18 nmol/cm^2

At 0.817 V (vs NHE) with overpotential 354 mV and current density (j, $mAcm^{-2}$), TOF is calculated as 5.23 s^{-1}

Quantitative measurements for evolved O_2:

A two compartments H-cell separated by a pretreated Nafion117 membrane is used for quantification of the evolved oxygen (O_2) by gas chromatograph (Thermo Trace GC-1110) equipped with a hayesep D and molecular sieve column with argon (Ar) as a carrier gas with a flow rate of 30 mL/min. The chromatograph is calibrated with known amount of gas mixture before the quantification. Three electrode set up is employed for the electrolysis where Ag/AgCl

and Pt coated titanium mesh are served as reference and counter electrode, respectively. For the working electrode, catalyst **1** is uniformly coated on a cleaned glassy carbon plate (geometrical surface area 1 cm^2 and the catalyst loading is 14μL i.e 56 μg). The working electrode is kept parallel to the counter electrode to achieve uniform voltage. 18 mL 0.1 M NaOH (pH 13) is used as electrolyte in each compartment of the H-cell. The electrolyte of the anode chamber is pre-saturated with argon (Ar) to remove dissolved oxygen for 30 minutes and the flow of argon gas is kept constant throughout the electrolysis with a flow rate of 6 mL/min which is directly connected to the gas chromatograph. After 20 minutes of electrolysis at 85V (NHE), the gas mixture is directly injected into the gas chromatograph and Oxygen (O_2) is detected by thermal conductivity detector (TCD). One more gas sample is injected into the gas chromatograph after saturated with argon before applying any potential to detect atmospheric oxygen present in the working electrode chamber.

Nafion117 membrane is washed with DI water for several times. Then it is heated at 80^{o}C for 1h in 3% H_2O_2 followed by another 2h boiling at same temperature in DI water. Then it is again boiled in 0.5M H_2SO_4 at same temperature. This pretreated nafion117 membrane is washed several times with DI water and stored in DI water at room temperature for further use.

The faradaic efficiency is calculated by using following formula[1]:

$$\% \text{ FE} = \frac{n * v * X * F * P}{R * T * i} * 100$$ where,

n = No of electron transferred i.e 4.

v = Flow rate of Argon.

X = Concentration of produced oxygen.

F = Faraday Constant, 96485 C/mol.

P = Ambient pressure, 1 atm.

R = Gas constant, 0.082 L. atm. $mol^{-1}.K^{-1}$

T = Temperature, 296K.

i = current at given sampling time.

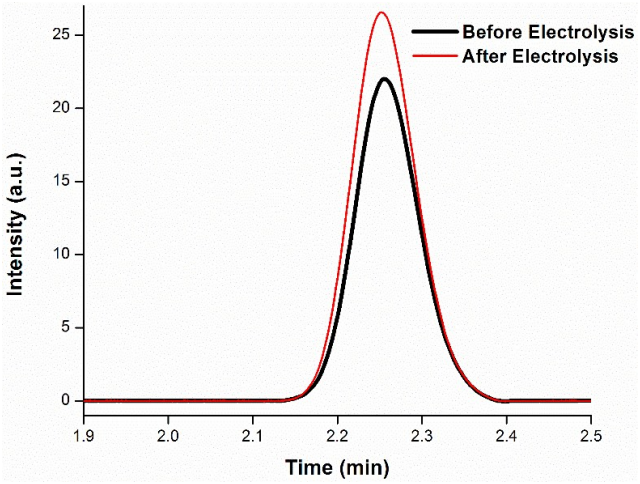


Figure S7: GC profiles of the quantitative calculation of the evolved O_2 before and after the catalysis.

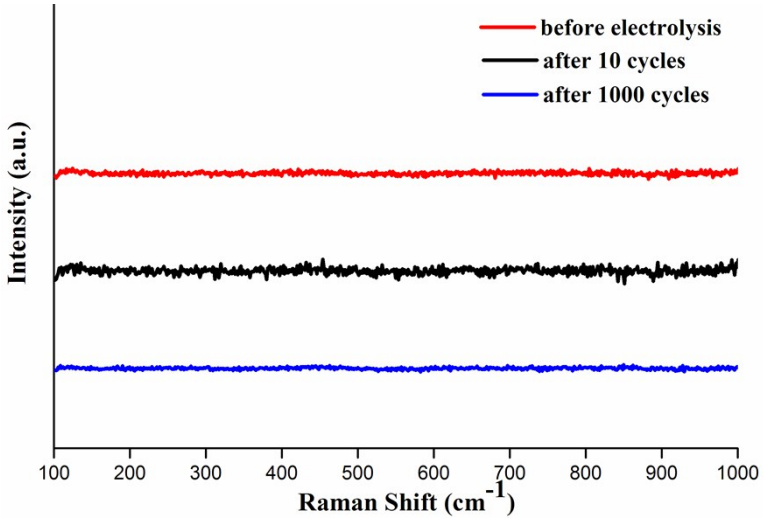
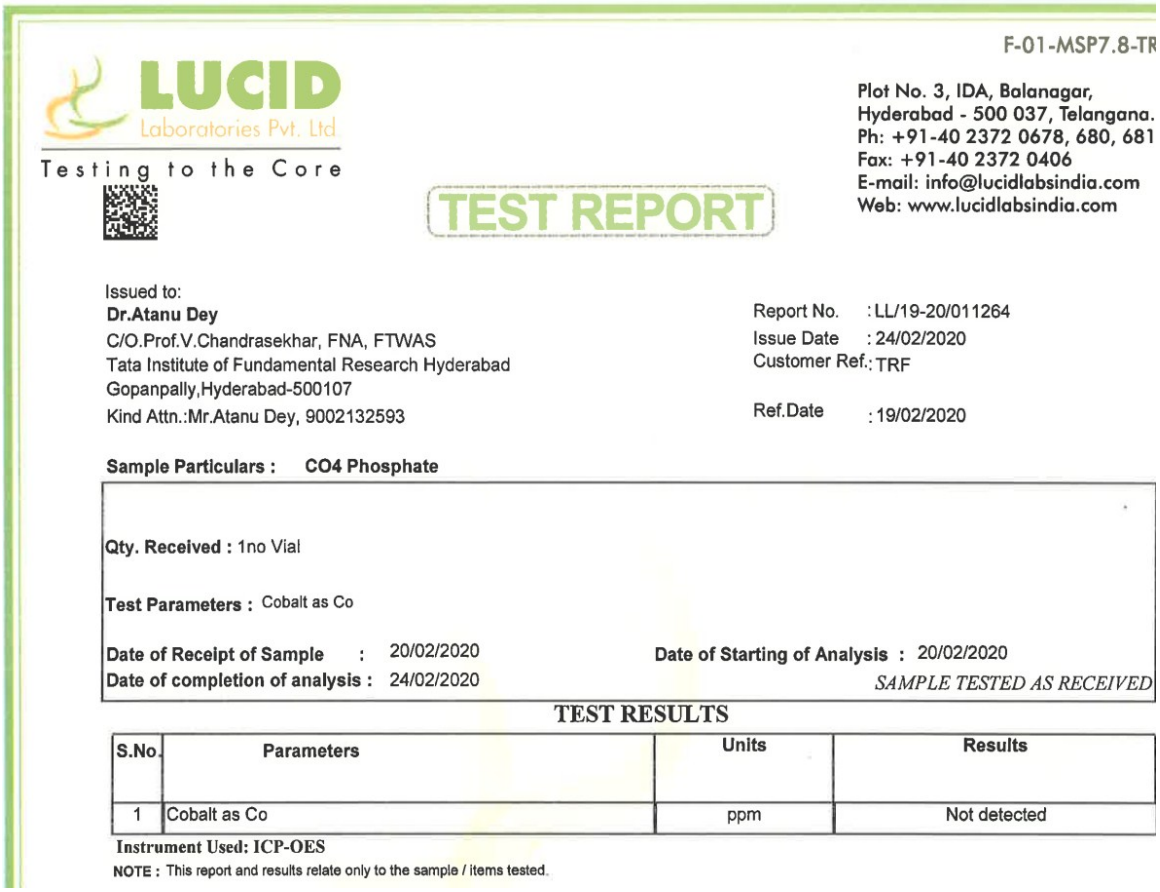


Figure S8: Raman spectra of the catalysts in different time intervals of the OER experiment. The absence of Raman signature of CoO_x rules out the possibility of the formation of CoO_x.



F-01-MSP7.8-TR

LUCID Laboratories Pvt. Ltd
Testing to the Core

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TEST REPORT

Issued to:
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C/O.Prof.V.Chandrasekhar, FNA, FTWAS
Tata Institute of Fundamental Research Hyderabad
Gopanpally,Hyderabad-500107
Kind Attn.:Mr.Atanu Dey, 9002132593

Report No. : LL/19-20/011264
Issue Date : 24/02/2020
Customer Ref.: TRF
Ref.Date : 19/02/2020

Sample Particulars : CO4 Phosphate

Qty. Received : 1no Vial

Test Parameters : Cobalt as Co

Date of Receipt of Sample : 20/02/2020
Date of Starting of Analysis : 20/02/2020
Date of completion of analysis : 24/02/2020
SAMPLE TESTED AS RECEIVED

TEST RESULTS

S.No.	Parameters	Units	Results
1	Cobalt as Co	ppm	Not detected

Instrument Used: ICP-OES

NOTE : This report and results relate only to the sample / items tested.

Figure S9: ICP analysis of the electrolyte solution after 1000 cycle durability test.

References:

1. *ACS Catal*. 2018, **8**, 6255−6264.

Table 1. Selected bond lenghts (Å) and angles (°) in complex **1**.

bond lengths around cobalt (1)	**bond lengths around cobalt (2)**
Co(1)-O(10) 1.921(2)	Co(2)-O(14) 1.963(2)
Co(1)-O(3) 1.925(2)	Co(2)-O(11) 1.904(2)
Co(1)-O(7) 1.915(2)	Co(2)-O(6) 1.925(2)
Co(1)-N(1) 2.039(3)	Co(2)-N(2) 2.035(3)
bond lengths around cobalt (3)	**bond lengths around cobalt (4)**
Co(3)-O(16) 1.967(2)	Co(4)-O(15) 1.976(2)
Co(3)-O(4) 1.918(2)	Co(4)-O(2) 1.932(2)
Co(3)-O(8) 1.921(2)	Co(4)-O(12) 1.918(2)
Co(3)-N(3) 1.997(2)	Co(4)-N(4) 2.036(2)

bond angles around cobalt (1)	**bond angles around cobalt (2)**
O(10)-Co(1)-O(3) 109.62(9)	O(14)-Co(2)-N(2) 102.12(10)
O(10)-Co(1)-N(1) 108.68(9)	O(11)-Co(2)-O(14) 110.45(9)
O(3)-Co(1)-N(1) 100.88(10)	O(11)-Co(2)-O(6) 115.57(9)
O(7)-Co(1)-O(10) 110.65(9)	O(11)-Co(2)-N(2) 102.93(10)
O(7)-Co(1)-O(3) 123.07(9)	O(6)-Co(2)-O(14) 121.78(8)
O(7)-Co(1)-N(1) 102.42(10)	O(6)-Co(2)-N(2) 100.36(10)
bond angles around cobalt(3)	**bond angles around cobalt(4)**
O(16)-Co(3)-N(3) 121.95(9)	O(15)-Co(4)-N(4) 102.26(9)
O(4)-Co(3)-O(16) 100.96(8)	O(2)-Co(4)-O(15) 119.40(8)
O(4)-Co(3)-O(8) 124.61(10)	O(2)-Co(4)-N(4) 99.72(10)
O(4)-Co(3)-N(3) 110.29(10)	O(12)-Co(4)-O(15) 111.24(9)
O(8)-Co(3)-O(16) 100.17(8)	O(12)-Co(4)-O(2) 118.62(9)
O(8)-Co(3)-N(3) 100.37(10)	O(12)-Co(4)-N(4) 101.18(10)

Table 2. Selected bond lenghts (Å) and angles (°) in complex **2**.

bond lengths around cobalt	selected bond angles
Co(1)-O(3)^1 2.046(2)	O(3)^1-Co(1)-O(3) 180.0
Co(1)-O(3) 2.046(2)	O(3)^1-Co(1)-O(5) 89.53(9)
Co(1)-O(5) 2.110(2)	O(3)^1-Co(1)-O(5)^1 90.47(9)
Co(1)-O(5)^1 2.110(2)	O(3)-Co(1)-O(5)^1 89.53(9)
Co(1)-N(1)^1 2.104(2)	O(3)-Co(1)-O(5) 90.47(9)
Co(1)-N(1)^1 2.104(2)	O(3)^1-Co(1)-N(1)^1 88.73(9)
	O(3)-Co(1)-N(1)^1 91.27(9)
	O(3)^1-Co(1)-N(1) 91.27(9)
	O(3)-Co(1)-N(1) 88.73(9)
	O(5)-Co(1)-O(5)^1 180.0
	N(1)-Co(1)-O(5)^1 88.06(10)
	N(1)^1-Co(1)-O(5) 88.06(10)
	N(1)-Co(1)-O(5) 91.94(10)
	N(1)^1-Co(1)-O(5)^1 91.94(10)
	N(1)^1-Co(1)-N(1) 180.00(13)