

Supporting Information (SI)

Estimation of Electrochemical Active Site Density of Metal-free Carbon-based Catalyst Using Phosphomolybdate (PMo_{12}) as an Adsorbate

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1. DC voltammograms in different conditions

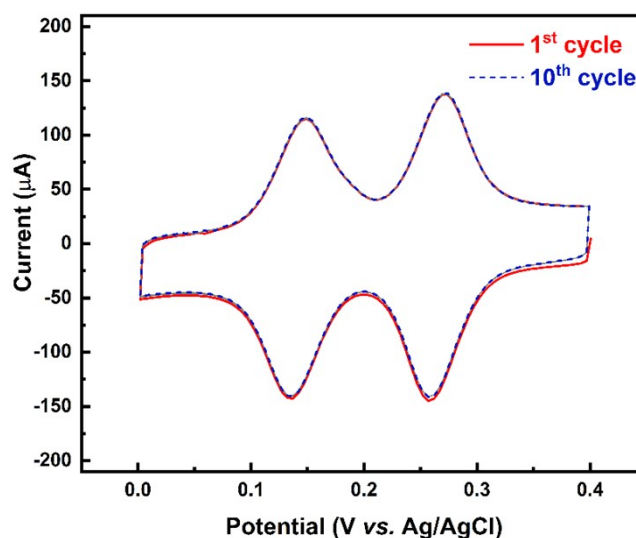


Figure S1 Cyclic voltammograms (CVs) (solid line 1st cycle and dotted line 10th cycle) on N/C-900 modified glassy carbon disk (GCD) electrode in argon-saturated 1 mM PMo_{12} in 0.5 M H_2SO_4 -50% dioxane recorded at a scan rate of 20 mV s^{-1} .

To ensure the complete coverage of the active sites by the adsorbate molecules (PMo_{12}), the carbon-modified glassy carbon disk electrode was cycled in 1mM PMo_{12} containing 0.5 M H_2SO_4 -50% dioxane electrolyte for 10 cycles. Since the peak currents of the 1st and 10th cycles do not show any significant difference, the electrode was cycled 10 times in the PMo_{12} containing electrolyte.

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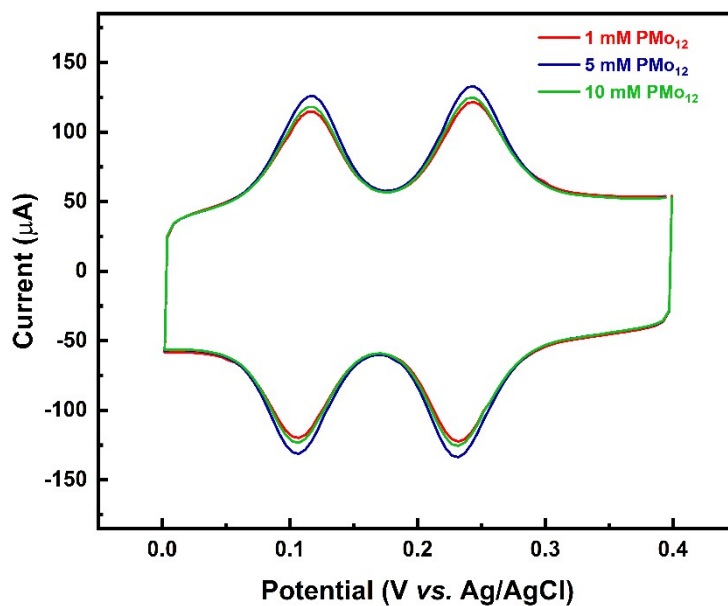


Figure S2 CVs on N/C-900 modified PMo_{12} adsorbed electrode recorded in PMo_{12} free argon-saturated 0.5 M H_2SO_4 -50% dioxane, after adsorption of the probe molecule from PMo_{12} solutions of different concentrations (1 mM, 5 mM, and 10 mM), recorded at a scan rate of 20 mV s^{-1} .

Figure S2 shows the voltammograms on PMo_{12} adsorbed N/C-900 electrode in solutions of PMo_{12} of different concentrations (1 mM, 5 mM, and 10 mM PMo_{12} in 0.5 M H_2SO_4 -50% dioxane). Comparable peak currents in the voltammograms indicate that the active sites are completely covered by the adsorbate molecules even at the low (1 mM) concentration. Therefore, 1 mM PMo_{12} concentration was used to adsorb the probe molecule.

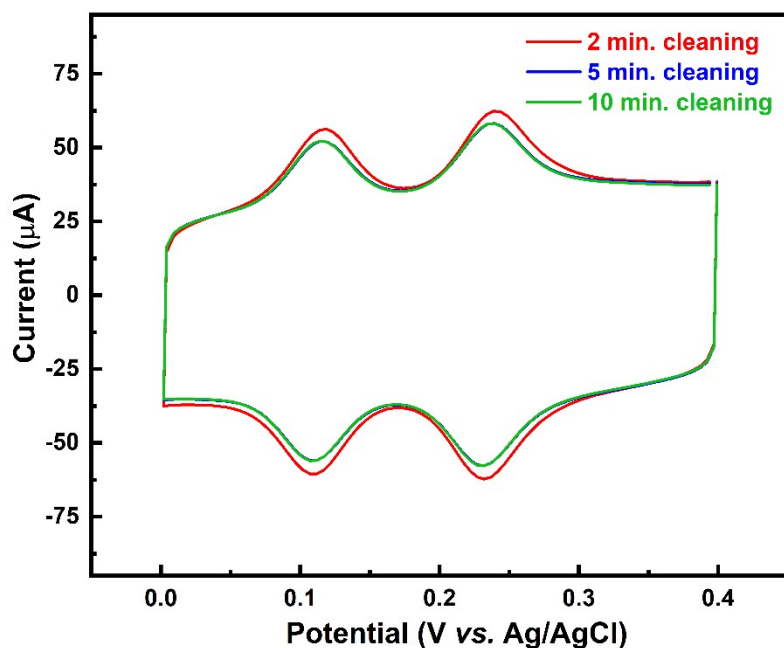


Figure S3 CVs on PMo_{12} adsorbed N/C-900 electrode in PMo_{12} free argon-saturated 0.5 M H_2SO_4 -50% dioxane after different cleaning time in DI water, recorded at a scan rate of 20 mV s^{-1} .

To remove the unbound/loosely bound adsorbate molecules, the electrode was rotated in the DI water for different durations (2, 5, and 10 minutes). The loosely bound molecules were removed within 5 minutes of rotation in the DI water. Hence, no change in the redox reaction peak current of the adsorbed PMo_{12} was observed after 5 minutes of cleaning. Therefore, 10 minutes cleaning time was used throughout the experiment.

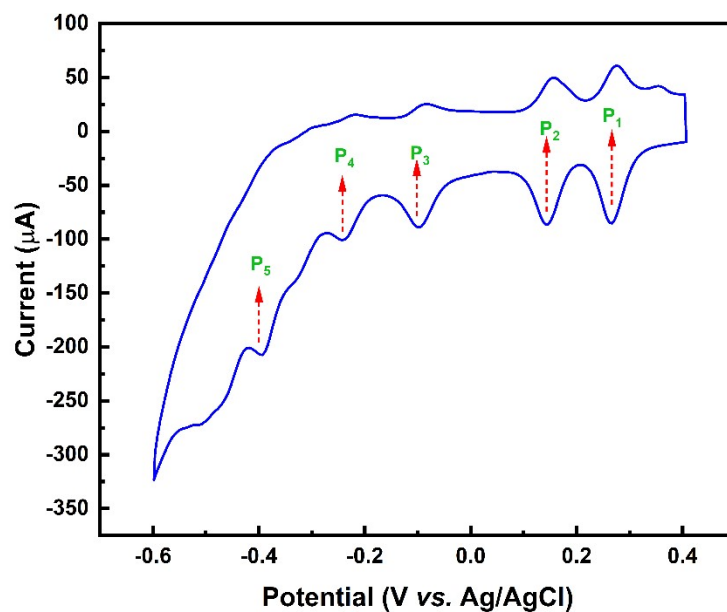


Figure S4 Cyclic voltammograms (CVs) on N/C-900 modified glassy carbon disk (GCD) electrode in argon-saturated 1 mM PMo_{12} in 0.5 M H_2SO_4 -50% dioxane recorded at a scan rate of 20 mV s^{-1} .

The cyclic voltammogram of 1 mM PMo_{12} in 0.5 M H_2SO_4 -50% dioxane on carbon-modified GCD electrode in the potential range of 0.4 – -0.6 V shows five (two proton-coupled electron-transfer) redox peaks.¹

2. Estimation of conversion factor (C.F)

To estimate the ECSA of Vulcan XC-72 carbon catalyst, a conversion factor using the PMo_{12} adsorption charge on the glassy carbon disk electrode of known geometric area was used. A correlation between the active site density and ECSA is established.

$$\text{Charge due to redox reaction of } \text{PMo}_{12} \text{ on the GCD} = 9.54 \times 10^{-6} \text{ C} \quad (\text{S1})$$

$$\text{Geometric area of glassy carbon disk electrode} = 0.196 \text{ cm}^2 \quad (\text{S2})$$

$$\text{Adsorption charge per unit area} = \frac{9.54 \times 10^{-6} \text{ C}}{0.196 \text{ cm}^2} = 4.867 \times 10^{-6} \text{ C cm}^{-2} \quad (\text{S3})$$

$$\text{Conversion factor (C.F)} = 4.867 \times 10^{-6} \text{ C cm}^{-2} \quad (\text{S4})$$

The adsorption charge of porous electrode of any different carbon loading divided by the C.F will give the ECSA.

$$ECSA \text{ of carbon catalyst} = \frac{6.17 \times 10^{-5}}{4.867 \times 10^{-6} C cm^{-2} \times 11 \times 10^{-6} (g)} = 10.87 m^2 g^{-1}$$

(S5)

3. MECSim simulations and data analysis

To estimate the S_D from the large-amplitude FTacV, the experimental data were compared with the MECSim simulations. All the parameters used in the MECSim simulations were the same as that in the experiments. Step by step method for the MECSim simulation is explained in the supplementary information of the reference 2.² However, the input file (master.sk) was modified as per the experimental conditions employed in the present work. The input parameters used in the MECSim simulations are explained below.

3.1 Solution resistance (R_s)

The solution resistance used in the MECSim simulation was obtained from the electrochemical impedance spectroscopy measurements. The EI spectra at 0.4 V were recorded in the PMO_{12} free electrolyte. Since no faradaic process happens at 0.4 V, a slightly tilted straight line was observed. The EI spectra were fitted with an equivalent circuit consisting of a resistance in series with a constant phase element (RQ).

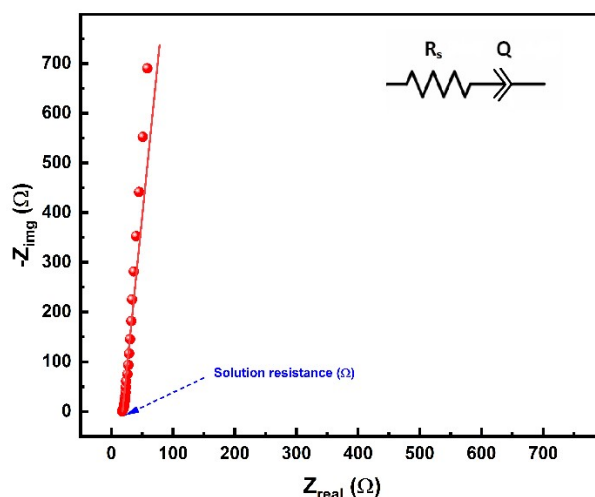


Figure S5 EIS patterns recorded in the double layer region (at 0.4 V vs. Ag/AgCl) on carbon-modified GCD electrode in the frequency range of 100 kHz ~ 100 mHz in argon-saturated 0.5 M H_2SO_4 -50% dioxane solution. The symbols and solid lines show the experimental and the fitted data, respectively.

3.2 Number of data points

A sufficient number of data points (5128) were recorded by the instrument to perform the fast Fourier analysis. The time difference between two consecutive data points was always constant ($\frac{200 \text{ sec}}{5128} = 39 \text{ m sec}$); therefore, no ringing effect was observed. The MECSim input parameter was modified accordingly.

		Time (s)	Current (μA)
► t	1	0.03894	188.82
	2	0.07794	201.66
	3	0.11694	212.96
	4	0.15594	221.96
	5	0.19494	229.13
	6	0.23394	233.88
	7	0.27294	235.88
	8	0.31194	233.65
	9	0.35094	227.48
	10	0.38994	217.4
	11	0.42894	203.63
	12	0.46794	187.19
	13	0.50694	168.72
	14	0.54594	147.81
	15	0.58494	125.33
	16	0.62394	100.8

3.3 Surface coverage (Γ)

Surface coverage (mol cm^{-2}) obtained from the DC voltammetry was used as an initial guess in the MECSim simulation. Thereafter, it was changed until a good agreement was observed between experimental and simulated data.

3.4 Reaction scheme

Since the adsorbed molecules are surface confined, the following reaction scheme was used in the MECSim simulations.



3.5 Double layer capacitance (C_{dl} (F cm^{-2}))

The double layer capacitance was obtained from the background voltammogram recorded in PMo_{12} free electrolyte in the potential range of 0.4 – 0.0 V at a scan rate of 20 mV s^{-1} .

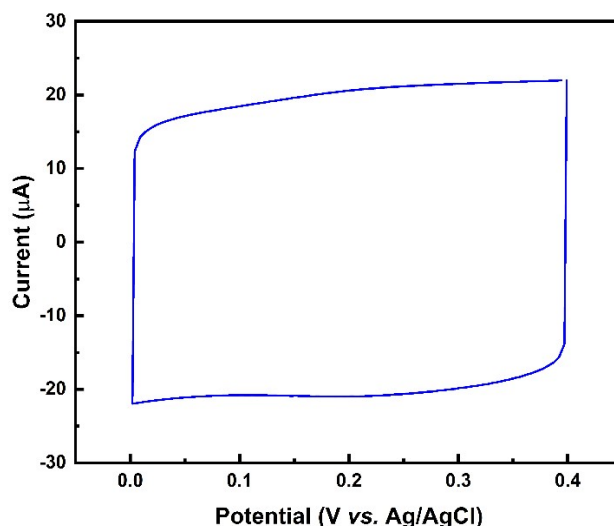


Figure S6 CV of carbon-modified GCD in argon-saturated 0.5 M H₂SO₄-50% dioxane solution, recorded at a scan rate of 20 mV s⁻¹.

3.6 Charge-transfer coefficient (α)

The charge-transfer coefficient (α) was always assumed 0.5 for all the simulations.

3.7 Heterogeneous rate coefficient (k^0)

The heterogeneous rate constant (k^0) of redox reactions of surface confined PMo₁₂ is very high ($\sim 10^4$ sec⁻¹).³ Moreover, to avoid the effect of k^0 on the kinetics of redox reaction of surface confined PMo₁₂, 10^4 sec⁻¹ k^0 value was used in the MECSim simulations.

4. FTacV measurement and data analysis

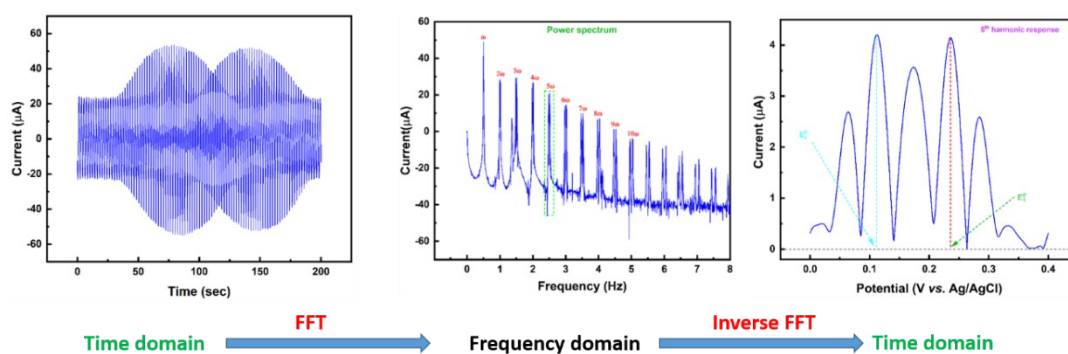


Figure S7 Illustration of FTacV measurement and data analysis

Table ST1 Solution resistance (R_s), double layer capacitance (C_{dl}), and surface coverage (Γ) values used in the MECSim simulations of large-amplitude FTacV

Catalyst	Catalyst loading (μg)	Solution resistance (R_s) (Ω)	Double layer capacitance (C_{dl}) ($\times 10^{-3} \text{ F cm}^{-2}$)	Surface coverage (Γ) ($\times 10^{-10} \text{ moles cm}^{-2}$)
GCD	-	13.6	0.43	0.07
N/C-900	26	15.8	5.00	8.0
Carbon	11	16.9	1.15	0.7
Carbon	16	16.4	1.22	1.2
Carbon	20	14.1	1.42	2.0
Carbon	26	13.7	1.54	3.7
Carbon	35	13.4	2.22	4.0

Table ST2 Number of active sites of nitrogen-doped carbon (N/C-900) at various loadings estimated from the background corrected DC voltammograms

N/C-900 loading (μg)	Total number of active sites ($\times 10^{14}$ sites)
16	18.8
20	20.2
26	22.3
35	25.2

Table ST3 Nitrogen content present in the C and N/C-900 samples obtained from XPS and CHN analysis.

Catalyst	Atomic wt% of N		
	from XPS	from CHN	reference
Carbon	—	0.1	This work
Carbon	—	0.1	Das et. al ⁴
N/C-900	1.31	1.61	This work
N/C-900	1.42	1.80	Das et. al ⁴

5. Physical characterizations

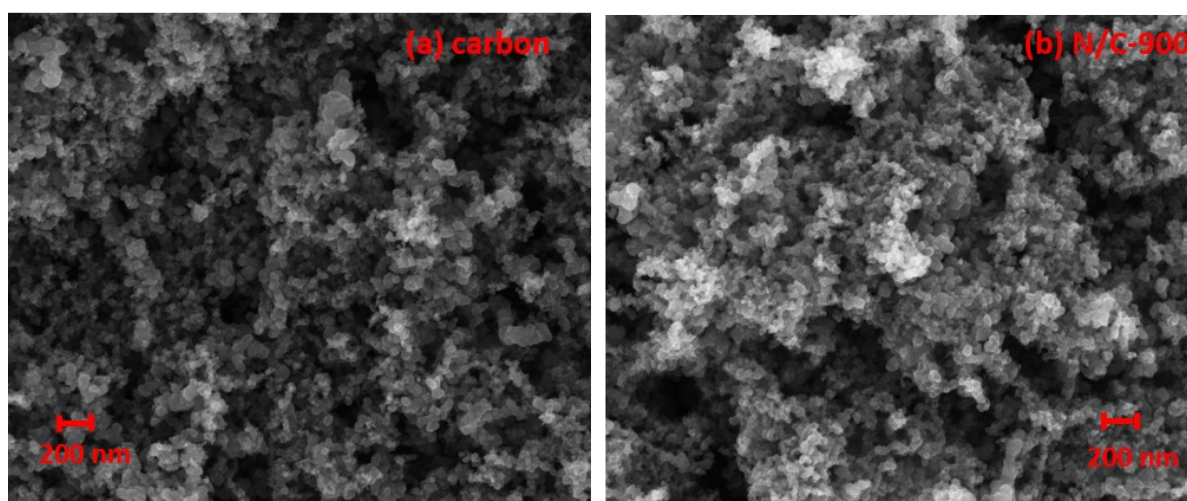


Figure S8 SEM images of (a) carbon and (b) N/C-900 catalysts

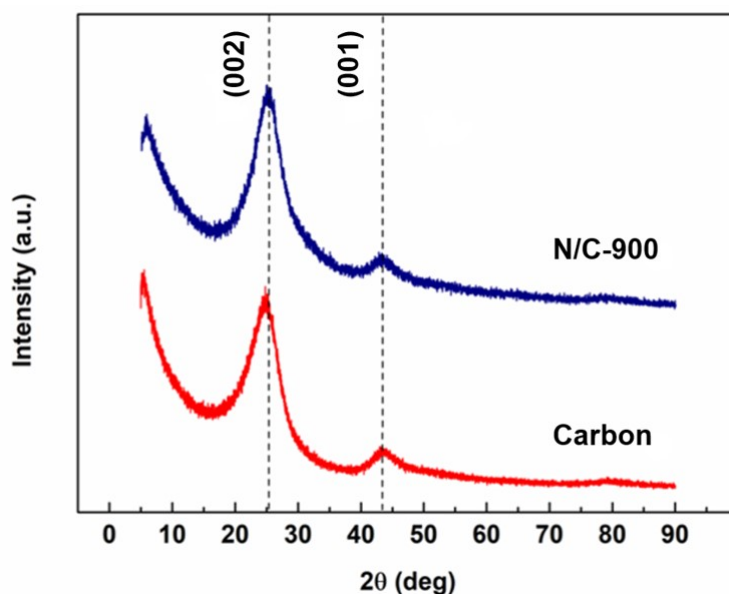


Figure S9 XRD patterns of carbon and nitrogen-doped carbon (N/C-900)

Since the doping atom percentage (nitrogen $\sim 1\%$) in the catalyst is very less, surface morphological and structural changes are negligible. This is apparent from the SEM images (Figure S8) and the XRD patterns (Figure S9). The two broad peaks in the XRD patterns of carbon and N/C-900 at $\sim 25^\circ$ and $\sim 43^\circ$ are attributed to the reflections from the graphite (002) and (001) planes of Vulcan XC-72 carbon, respectively. This suggests that the surface defects, dangling bonds and unsatisfied carbon valences, due to presence of unintentional metal content in the catalyst matrix, are the active site of the carbon-based catalyst. These surface defects,

dangling bond and unsatisfied valences increase after doping the carbon with nitrogen; therefore, an increase in the active site density is observed.

References

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2. Snitkoff-Sol, R. Z.; Friedman, A.; Honig, H. C.; Yurko, Y.; Kozhushner, A.; Zachman, M. J.; Zelenay, P.; Bond, A. M.; Elbaz, L. Quantifying the electrochemical active site density of precious metal-free catalysts in situ in fuel cells. *Nat. Catal.* **2022**, *5*, 163–170.
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