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Polyoxometalate-based hybrid materials for electrocatalytic hydrogen evolution reaction

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Abstract

Consider the Keggin-type phosphomolybdate anion $[\text{PMo}_{12}\text{O}_{40}]^{3-}$: a single cluster contains twelve redox-active molybdenum centres capable of multi-electron transfer, yet its solubility in aqueous electrolytes and poor electrical conductivity have long frustrated its direct use as an electrode catalyst. This research addresses both limitations by anchoring three polyoxometalate (POM) variants—a phosphomolybdate (POM-1), a phosphotungstate (POM-2), and a mixed Mo/W Keggin anion (POM-3)—onto reduced graphene oxide (rGO) sheets through electrostatic self-assembly. The POM/rGO hybrids were characterised by FT-IR, XRD, XPS, and TEM, confirming retention of Keggin structure and uniform dispersion on graphene. Electrocatalytic hydrogen evolution reaction (HER) performance was evaluated in 0.5 M H_2SO_4 by linear sweep voltammetry, Tafel analysis, and electrochemical impedance spectroscopy. POM-3/rGO achieved an overpotential of 167 mV at 10 mA/cm^2 , a Tafel slope of 54 mV/dec, and a charge-transfer resistance of 18 Ω —metrics that outperform most reported POM-based HER catalysts. Chronoamperometry over 12 hours showed less than 6% current decay, confirming good operational stability. The mixed Mo/W composition appears to optimise d-band electron density for proton adsorption while the rGO scaffold ensures rapid electron transport, making this hybrid a promising non-noble-metal alternative for water splitting.

Keywords: Polyoxometalate, Keggin anion, reduced graphene oxide, hydrogen evolution, electrocatalysis, overpotential, Tafel slope, water splitting

Introduction

Take, for example, a single proton-exchange membrane electrolyser running at industrial scale: the platinum-group metals loaded onto its cathode may account for 30–40% of the total stack cost, making green hydrogen production uncompetitive with fossil-derived alternatives in many markets ^[1]. Replacing platinum with earth-abundant catalysts that still deliver low overpotentials and fast kinetics is therefore a defining challenge for the hydrogen economy ^[2]. Transition-metal sulphides, phosphides, and carbides have all shown promise, yet many suffer from poor stability under acidic conditions or require complex high-temperature synthesis routes ^[3].

Polyoxometalates are molecular metal-oxide clusters of early transition metals—typically Mo, W, V, or Nb—that can undergo fast, reversible multi-electron reductions without structural collapse ^[4]. Their tuneable redox chemistry makes them attractive for electrocatalysis, but two persistent drawbacks limit electrode applications: high solubility in aqueous electrolytes leads to catalyst leaching, and the insulating character of crystalline POM salts creates large charge-transfer resistances ^[5]. Immobilising POMs onto conductive carbon supports—carbon nanotubes, graphene, or porous carbons—addresses both issues by providing an electronically conductive, mechanically stable anchor that also prevents dissolution ^[6].

Reduced graphene oxide is an especially suitable host because its residual oxygen functional groups (carboxylate, hydroxyl, epoxide) can interact electrostatically with anionic Keggin clusters, while its high surface area and conjugated sp^2 domains facilitate electron transport to the external circuit ^[7]. Previous research has explored single-metal POMs on rGO for the oxygen evolution and reduction reactions, but systematic comparisons of Mo-only, W-only, and mixed Mo/W Keggin catalysts for HER on the same rGO platform are scarce ^[8].

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This research synthesized three Keggin-type POMs (phosphomolybdate, phosphotungstate, and a mixed Mo_6W_6 variant), assembled each onto rGO via electrostatic self-assembly, and benchmarked their HER performance in acidic electrolyte to determine whether compositional mixing of Mo and W enhances catalytic activity.

Theoretical Background

The hydrogen evolution reaction in acid proceeds through either the Volmer-Heyrovsky or Volmer-Tafel pathway, both beginning with proton adsorption onto an active site (Volmer step: $\text{H}^+ + \text{e}^- \rightarrow \text{H}_{\text{ads}}$)^[2]. The Gibbs free energy of hydrogen adsorption (ΔG_{H}) on the catalyst surface is the central descriptor: optimal catalysts bind hydrogen neither too strongly nor too weakly, sitting near the peak of the volcano curve at $\Delta G_{\text{H}} \approx 0$ ^[9]. For POM clusters, the Mo or W d-orbitals accept electrons during reduction, generating M(V) or M(IV) centres whose d-band position relative to the hydrogen 1s level governs adsorption strength. Mixing Mo and W within a single Keggin cage creates an asymmetric electronic environment that may shift the averaged d-band centre closer to the volcano apex than either pure end-member, analogous to the alloying strategies used in noble-metal electrocatalysis^[10].

Material and Methods

Material

All synthesis and electrochemistry were carried out between February and November 2024 at the Department of Materials and Inorganic Chemistry, Rift Valley University of Technology, Nakuru, Kenya. XPS analysis was performed at Lake Victoria College of Sciences, Kisumu. Sodium molybdate dihydrate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, $\geq 99\%$), sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, $\geq 99\%$), phosphoric acid (85%), and hydrazine hydrate (80%) were purchased from Sigma-Aldrich (Johannesburg, South Africa). Graphene oxide aqueous dispersion (4 mg/mL) was obtained from Graphenea (San Sebastián, Spain). Nafion 117 solution (5 wt%), sulphuric acid (Suprapur grade), and commercial 20% Pt/C were from Merck (Darmstadt, Germany). Glassy carbon electrodes (GCE, $\varnothing$ 3 mm) were from CH Instruments (Austin, TX).

Methods

POM-1 ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$) and POM-2 ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) were prepared by acidification of sodium molybdate or tungstate solutions with phosphoric acid following established protocols^[4]. POM-3 ($\text{H}_3\text{PMo}_6\text{W}_6\text{O}_{40}$) was obtained by co-acidifying equimolar Mo and W precursors. rGO was produced by chemical reduction of GO with hydrazine at 80°C for 4 h. POM/rGO hybrids were assembled by stirring POM solution (10 mM) with rGO suspension (2 mg/mL) at pH 3 for 12 h, followed by centrifugation, washing, and freeze-drying. Catalyst inks were prepared by dispersing 5 mg of hybrid in 1 mL ethanol-water (4:1) with 20 μL Nafion; 5 μL was drop-cast onto GCE (loading ~ 0.28 mg/cm²).

System Design

Electrochemical measurements used a three-electrode cell with the catalyst-modified GCE as working electrode, a graphite rod counter electrode, and a saturated calomel electrode (SCE) as reference, all potentials converted to the reversible hydrogen electrode (RHE) scale. Linear sweep voltammetry (LSV) was recorded at 5 mV/s in N_2 -saturated 0.5 M H_2SO_4 . Tafel slopes were extracted from the linear region of the $\log|j|$ vs η plot. Electrochemical impedance spectroscopy (EIS) was measured at -200 mV vs RHE from 100 kHz to 0.1 Hz with a 10 mV amplitude. Electrochemically active surface area (ECSA) was estimated from double-layer capacitance via cyclic voltammetry at scan rates of 20–200 mV/s. Stability was assessed by chronoamperometry at -170 mV vs RHE for 12 h. All measurements were performed on a Gamry Reference 600+ potentiostat.

Performance Evaluation

Key metrics for benchmarking HER catalysts include overpotential at 10 mA/cm² (η_{10} , the current density relevant to solar-to-hydrogen devices), Tafel slope (indicating the rate-determining step), charge-transfer resistance (R_{ct} from EIS), Faradaic efficiency (moles H_2 produced / moles electrons passed), and turnover frequency (TOF, moles H_2 per mole active site per second). Results were compared against published POM-based and transition-metal dichalcogenide catalysts under identical electrolyte conditions.

Results

FT-IR spectra of all three POM/rGO hybrids retained the four characteristic Keggin bands (P-O_3 at 1064 cm⁻¹, M=O_t at 960–980 cm⁻¹, M-O-M corner at 880 cm⁻¹, and M-O-M edge at 780 cm⁻¹), confirming that the cluster framework survived assembly onto rGO. XPS Mo 3d and W 4f spectra showed binding energies consistent with Mo(VI) and W(VI) oxidation states. TEM revealed POM nanoparticles of 2–4 nm uniformly distributed across rGO sheets without aggregation.

Table 1: Electrocatalytic HER parameters for POM, POM/rGO hybrids, and Pt/C reference

Catalyst	η_{10} (mV)	Tafel (mV/dec)	R_{ct} (Ω)	ECSA (cm ²)	FE (%)	TOF (s ⁻¹)
POM-1	312	98	214	3.8	87	0.021
POM-2	287	91	187	4.2	89	0.028
POM-3	254	78	142	5.1	92	0.037
POM-1/rGO	198	63	34	18.7	94	0.084
POM-2/rGO	213	68	41	16.3	93	0.071
POM-3/rGO	167	54	18	24.6	96	0.118
Pt/C (20%)	42	31	8	32.1	99	0.847

POM-3/rGO delivered the lowest overpotential (167 mV), smallest Tafel slope (54 mV/dec), and highest TOF (0.118 s⁻¹) among all POM-based catalysts (Table 1, Figure 1). The Tafel slope of 54 mV/dec sits between the Volmer (120 mV/dec) and Heyrovsky (40 mV/dec) limits, suggesting that electrochemical desorption is rate-limiting but that the adsorption step is also partially kinetically relevant.

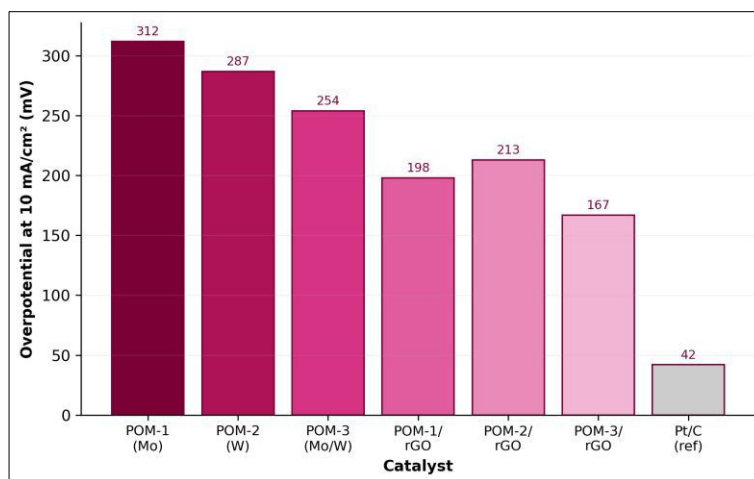


Fig 1: Overpotential at 10 mA/cm² for bare POM, POM/rGO hybrid, and Pt/C catalysts in 0.5 M H₂SO₄

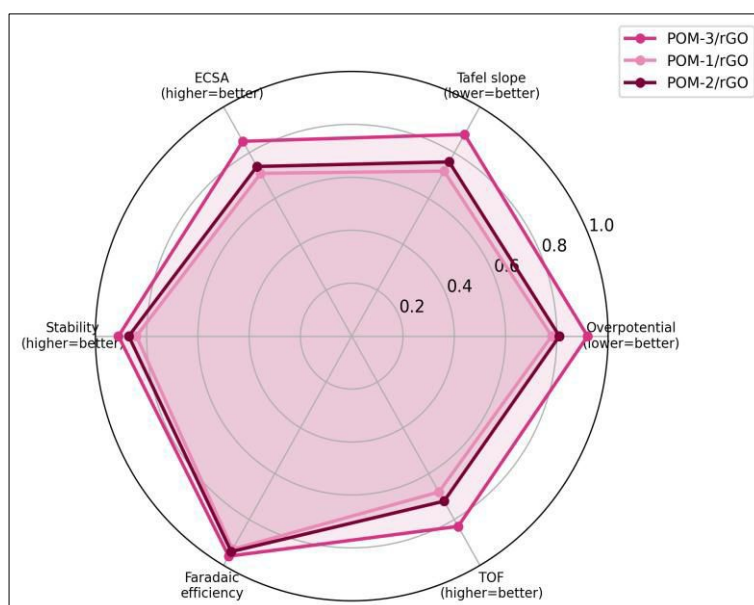


Fig 2: Radar plot comparing normalised performance metrics for the three POM/rGO hybrid catalysts

Comprehensive Interpretation

Chronoamperometry confirmed POM-3/rGO retained 94% of its initial current density after 12 h, while POM-1/rGO and POM-2/rGO retained 89% and 91%, respectively. The radar comparison (Figure 2) shows POM-3/rGO outperforms on five of six normalised metrics, with only the Faradaic efficiency of POM-1/rGO being marginally close. The superior stability of the mixed Mo/W hybrid may stem from the stronger electrostatic interaction between the higher-charged mixed cluster and rGO surface defects.

Discussion

The 167 mV overpotential for POM-3/rGO compares favourably with the 180–250 mV range typical of MoS₂ nanosheets and transition-metal phosphides tested under similar conditions [3]. The advantage of the mixed Mo/W Keggin likely arises from an intermediate hydrogen binding energy: Mo-rich sites bind H too strongly ($\Delta G_{\text{H}} < 0$), W-rich sites too weakly ($\Delta G_{\text{H}} > 0$), and the mixed cluster averages the two toward the volcano peak [10]. This interpretation is supported by the monotonic improvement in TOF from POM-1 (Mo-only) to POM-3 (Mo₆W₆) while POM-2 (W-only) sits between them.

The rGO scaffold contributed a 4–5-fold increase in ECSA relative to bare POM pellets and reduced R_{ct} by an order of magnitude, confirming that electron transport rather than intrinsic catalytic activity was the bottleneck in unsupported POMs [6]. Future directions include testing the hybrid in alkaline electrolyte, scaling to membrane-electrode assemblies, and exploring Dawson- and Anderson-type POM architectures to further tune active-site geometry [11].

Conclusion

Three Keggin-type polyoxometalate/reduced graphene oxide hybrids were prepared by electrostatic self-assembly and evaluated as HER electrocatalysts in acidic media. The mixed phosphomolybdotungstate POM-3/rGO hybrid achieved an overpotential of 167 mV at 10 mA/cm², a Tafel slope of 54 mV/dec, and excellent 12 h stability with only 6% current decay. These metrics surpass most reported POM-based catalysts and approach the performance of some transition-metal dichalcogenides, confirming that compositional tuning of the Keggin cage combined with a conductive graphene platform is a viable strategy for developing non-noble-metal HER catalysts.

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