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Polyoxometalates (POMs): from Electroactive Clusters to Energy MaterialsView Article Online
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*Michael Horn¹, Amandeep Singh¹, Suaad Alomari¹, Sara Goberna-Ferrón², Raúl Benages-Vilau²,
Nilesh Chodankar³, Nunzio Motta^{1, 4}, Ken (Kostya) Ostrikov^{1, 4}, Jennifer MacLeod^{1, 4}, Prashant
Sonar^{1, 4}, Pedro Gomez-Romero^{2*}, Deepak Dubal^{1,4*}*

¹School of Chemistry and Physics, Queensland University of Technology (QUT), 2 George Street, Brisbane, 4000 Queensland, Australia.

²Catalan Institute of Nanoscience and Nanotechnology, ICN2 (CSIC-BIST) Campus UAB, E-08193 Bellaterra (Barcelona), Spain

³School of Chemical Engineering, Chonnam National University, Gwangju 500–757, South Korea

⁴Centre for Materials Science, Queensland University of Technology (QUT), 2 George Street, Brisbane, 4000 Queensland, Australia.

Abstract

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Polyoxometalates (POMs) represent a class of nanomaterials, which hold enormous promise for a range of energy-related applications. Their promise is owing to their “special” structure that gives POMs a truly unique ability to control redox reactions in energy conversion and storage. One such amazing capability is their large number of redox active sites that arises from the complex three-dimensional cluster of metal-oxide ions linked together by oxygen atoms. Here, a critical review on how POMs emerged from being molecular clusters for fundamental studies, to next-generation materials for energy applications is provided. We highlight how exploiting the versatility and activity of these molecules can lead to improved performance in energy devices such as supercapacitors and batteries, and in energy catalyst applications. The potential of POMs across numerous fields is systematically outlined by investigating structure-property-performance relationships and the determinant factors for energy systems. Finally, the challenges and opportunities for this class of materials with respect to addressing our pressing energy-related concerns are identified.

Broader context

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Unprecedented global energy demand and climate change have spawned broad based efforts to develop new sustainable clean energy conversion and storage technologies. A range of electrochemical energy systems have the potential to address critical energy demands, however, their performance is far from the expectations. To this end, particular emphasis has been given to the design and engineering of new functional materials. Polyoxometalates (POMs), a class of metal oxide cluster anions with the ability to reversibly transfer multi-electrons have recently broken through as functional materials. POMs exhibit unique chemical properties unlike those of general metal complexes with various ligands. The open frameworks with independent structural units and rich-redox chemistry makes them ideal materials for cutting-edge energy-related technologies. Here, we provide critical analysis of the current knowledge on the impact of structure and properties of POMs for improved performance in energy devices. We believe that this review will not only provide the fundamental knowledge in the field of POMs-for-Energy but will also help to address the current challenges in electrification to decarbonize industry and society.

1. Introduction

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Many countries around the world have set targets to limit anthropogenic climate change and with this comes an effort to reduce emissions that are the product of fossil fuel combustion.¹ This is driving a shift towards electrified transport systems, with urgent demand for improved energy storage; but these systems are only as clean as the source of the electricity they consume. Therefore, the transition towards energy *production* via renewable sources *as well as* efficient *storage*, are two inseparable parts of the net equation. Another trend seen in recent years is the rapid increase in portable electronics and electric devices for uses including communications, computing, sensing, entertainment, construction, and general maintenance.¹⁻⁴ A link between this trend climate change mitigation, is a very high demand for research and development of innovative electrical energy conversion and storage.

A wide range of energy conversion and storage technologies are being researched intensely. Various battery chemistries include lithium and sodium, and redox-flow.²⁻⁴ Other modes of conversion and storage include supercapacitors, hybrid battery-supercapacitors, fuel cells, hydrogen-based systems and a wide range of photovoltaics.⁵⁻¹⁰ The development of the next generation of all these modes requires materials that can be understood and controlled at the nanoscale, but also applied on the scale of industrial manufacturing processes.

Polyoxometalates (POMs) are an exceptional group of inorganic redox active materials that consist of multiple metal-oxide ions linked together by oxygen atoms to form nanoclusters within an ordered three-dimensional framework. Their size allows them to be viewed as a type of oxide quantum dots,^{11,12} possessing a very high surface to bulk ratio. Their rapid and highly reversible redox activity endows them with excellent electrochemical properties. This underpins the motivation for an increasing amount of research into POMs for energy materials and other related applications.

POMs have a history dating back to the late 1700s when heteropoly acids were first discovered. From the early 1800s their complex structure was the subject of theorizing.¹³ It was not until 1934 when J. F. Keggin used x-ray diffraction to interpret the structure of 12-phosphotungstic

acid,¹³ that some level of agreement about structure started to be reached. The general chemical form of the class of POMs to which 12-phosphotungstic acid belongs can be written $\text{XM}_{12}\text{O}_{40}$, where X denotes a heteroatom and M a transition metal addenda atom. This form is named after its discoverer and is referred to as the Keggin structure. It remains one of the most widely investigated and understood structural forms of POMs.

Part of the attraction to these metal oxide clusters relates to their broad range of possible redox states and valences, while the molecular cluster itself may experience very little change in its physical structure. For example, stable crystal forms of ionic POM compounds can be synthesized that possess the same stoichiometry in the POM anion, but the anion may carry a different charge. The salt $\text{K}_6[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$ forms green prismatic crystals. The Keggin POM anion in the compound carries a molecular charge of -6e (that is $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{-6}$). Under careful synthesis conditions, Casañ-Pastor et al. produced a novel potassium salt of the POM anion $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{-8}$.¹⁴ A solid crystalline product of the salt possessed a deep blue color. The authors describe how the extra two “blue electrons” hop between the (tungsten) metal atoms at the center of each tetrahedra that make up the cluster (see Figure 1 for a visualization of the tetrahedra forming a POM cluster). However, they also emphasize that molecular orbitals involving oxygen atoms play an important role in electron delocalization. Yet, despite the changes in valency, the bond lengths between the addenda atoms and other metal-oxygen bonds in the POM cluster change only on the order of a few percent of an Angstrom, and the cluster maintains a specific α type of Keggin structure (see Figure 1), that actually becomes more rigid. These features hint at the capability of POMs to act as stable and versatile molecular reservoirs for charge carriers.

The Keggin structure was the first stable complex form of POM to be characterized, but many other framework forms have been discovered since.⁵ The structural motifs can be broadly classified into two types, isopolyoxometalates (isopolyanions) and heteropolyoxometalates (heteropolyanions). The former case possesses all the metal atoms are of the same element, where the addenda metal atoms are accompanied by heteroatoms, which may be either metal or non-metal. Common

heteroatoms include W, Mo, V, C or Si, P, and As, whereas common addenda metals include Mo and W.¹⁵ The general formation reaction of POMs can be written as

where MO_4^{2-} is an oxyanion, and $M_xO_{4x-y}^{(2x-m)-}$ is an isopolyanion. In contrast to the formation of isopolyanions, if the condensation reaction of several (x) oxyanions occurs around (s) central heteroatoms the reaction leads to the formation of heteropolyanions with the general formula $X_sM_xO_y^{z-}$. Various kinetically driven structures can be formed with the number of metal atoms and heteroatoms having different X/M ratios. Knowledge of isopolyoxometalates is mostly derived from the Lindqvist ($[Mo_6O_{19}]^{2-}$), heptamolybdate ($[Mo_7O_{24}]^{6-}$) and decamolybdate anions.¹⁵ A much greater number of heteropolyoxometalates have been characterized. Based on their X/M ratio two fundamental types of hetero-POM structures are the Keggin ($X/M = \frac{1}{12}$) and Dawson ($X/M = \frac{2}{18}$) structures,^{[1]16} as shown in Figure 1. However many more have been identified such as the Dexter-Silverton structure ($[XM_{12}O_{42}]^{n-}$),¹⁷ and the much larger Keplerate cluster (Mo_{132} -based).¹⁸ Furthermore, isomeric variations to the basic structures exist; for example, the Keggin structure has five recognized isomeric variations (denoted α through to ϵ – see Figure 1). The wide range of structural forms, with various properties and tunability has prompted researchers to present libraries of known POMs as building blocks for nanomaterials.^{19,20} In addition to the synthesis and structural studies of larger and more intricate forms of these interesting nanoparticles (NPs), facile synthesis methods are sought which avoid the need for separation and purification of intermediate products.¹⁸ Thus, extensive work has gone into the optimization of POM synthesis routes, to improve the yield of specific moieties as well as minimizing time and cost.²¹ For a comprehensive and recent review of POM structures and synthesis, the reader is referred to the work of Gumerova et al.¹⁵

Herein, we have presented a brief history and discussion around the classification and properties of POM materials with primary focus on the energy-related applications (Figure 2). Specifically, we focus on the properties of heteropolyoxometalates and recent progress towards their

applications in supercapacitors (SCs), batteries and various catalytic applications. Firstly, the review highlights (section 2), the key advances in the enhancements of electrochemical supercapacitive properties by introducing POMs as redox active moieties that offers large numbers of electrons during the oxidation/reduction processes. The challenges of anchoring POMs to other hybridizing materials are presented with other interesting properties and theoretical insights to be used in energy-devices. Section 3 carries this subject matter forward into battery applications where POMs have been much more widely explored. Several battery chemistries such as lithium ion, sodium ion and redox flow systems are briefly discussed. The lithium ion chemistry is given greatest attention based on its popularity for research and the resulting depth of literature. This allows the article to present the major breakthroughs in stable attachment of POMs to conductive or chemically active electrode components, the use of POMs as precursors to other high surface area active materials, and POM hybrid materials for batteries. The following section goes into discussion of the science and engineering of POMs for catalysis applications (section 4). Research on POM-based catalysts has greatly increased in the last few years. Among the research fields, chemical oxygen reactions, such as for oxygen evolution (in electrolyzers) and for oxygen reduction (in fuel cells) represent a bottleneck for the development of energy conversion technologies. The section also includes a discussion on the progress of POM-based materials in different catalytic reactions such as carbon dioxide (CO₂) reduction, nitrogen (N₂) reduction and biomass conversion. Each section presents perspectives on the different roles for POMs in energy, including those which are expected to stimulate new research directions. The final section summarizes key points and conclusions as well as a short commentary on future challenges and the outlook for POMs.

2. POM-based Materials for Supercapacitors

Traditional supercapacitors (SCs) store charge via the electric double layer effect (EDL). In these devices, high surface area materials are exploited to store charge via the electrophysical separation over very small distances at an electrode-electrolyte interface. Relative to current battery

chemistries, these devices are able to deliver very high power densities but they suffer from low energy density.²² Over the last decade, a widely investigated challenge has been to increase the amount of energy that can be stored in supercapacitors, while not trading off too heavily against their high power capability and exceptionally long cycle life. The theoretical capacitance of graphene sets somewhat of a benchmark for this work, at 550 F.g⁻¹. The basis for this as a benchmark is rationalized by virtue of it representing a 100% exploited atomically thin surface, for the formation of an EDL.

In practice, research on purely EDL capacitive materials has achieved around as high as 200-300 F.g⁻¹.²³ However, aside from pursuing of the goal of maximal surface usage, a popular means of improving energy density is via pseudocapacitance (Note that the term pseudocapacitance represents the extrinsic pseudocapacitive behavior), where chemically active species undergo fast reversible redox reactions close to the surface of electrode materials.²⁴ POMs are great contender materials for such purpose, given their high surface-to-bulk ratio, and the numerous available redox states of the addenda metal species, which enable multi-electron charge transfer per molecule. However, there are major issues that remain to be addressed and comparison can be difficult given the wide variable space and range of metrics available for expressing results. Two of the greatest challenges for POMs are securely anchoring POMs to a host material and achieving the very long-term cycling stability. This section will discuss some advances that have been made towards all the above challenges, in applying POMs in SCs.

The idea of exploiting the multiple redox states of POMs for enhancing the energy density of SCs with near-surface confined redox reactions has been known for more than two decades. As far back as 1997, POMs were being combined with conducting polymers such as polypyrrole (PPY),²⁵ polyaniline (PANI)^{26,27} and poly(3,4-ethylenedioxythiophene) (PEDOT).²⁸ These materials were presented as organic-inorganic “hybrids”, and the focus was on their use in SCs. This work has continued in recent years, suggesting that there is much that remains to be explored and to be better understood.²⁹ In 2012, Gomez-Romero’s group conducted one of the earlier reported studies where a PMo₁₂-type POM was anchored to a simple activated carbon (AC) to create a hybrid material. The

hybrid exhibited significantly enhanced performance over bare AC as large current under the CV curves can be seen in Figure 3 (a).²⁸ Phosphomolybdic acid ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$) was used to decorate the AC, increasing its mass by 54%. The *cell capacitance* of the hybrid was improved by an average 27% over a range of current densities up to 3 A.g^{-1} and it displayed strong cycling stability with 91% retention over 8,000 cycles. Although the cell was symmetric, with the same materials and mass loading for each electrode, the capacitance for positive and negative were different (160 F.g^{-1} and 183 F.g^{-1} , respectively), suggesting that even greater performance can be achievable by refined cell construction and balancing (see Figure 3b). The authors compare their achievements to other work on POM-carbon nanotube-based hybrids,³⁰⁻³² citing improvements in every respect. Since then more work has reinforced that the energy density of microporous carbons can be improved by the hybridization with POM. The later work has added new knowledge about the connection to microporosity³³ and the ability of POM-based hybrids to enable high-voltage aqueous systems.³⁴

Straightforward approaches to applying POMs have been shown to yield good results. Vanadate POMs have been used as a positive electrode with AC as the negative electrode in the construction of an asymmetric device.³⁵ They reported 354 F.g^{-1} with 73 Wh.kg^{-1} at 0.1 A.g^{-1} and associated power of 312 W.kg^{-1} . As can be seen from the Ragone plot in Figure 3 (c), power could be increased to 6238 W.kg^{-1} but this resulted in a reduction of energy density to 22 Wh.kg^{-1} . The capacitance retention was 70% after 1000 cycles. In this above report, the POM based electrode was formed by simple mechanical hand mixing of the materials with a binder and carbon black. In battery research, mechanical methods of mixing POMs, such as this hand mixing, or ball milling and other techniques, are frequently reported, and described in section 3. More commonly in SCs, various solution-based chemistry approaches are applied to anchor the POMs on conducting scaffold to use as an electrode.

Exotic emerging materials have also been used for anchoring POMs. For example, metallacalixarenes that are ordered crystalline materials similar to 2D metal organic frameworks (MOFs) with repeating nano-sized cup-shaped pockets in their surface (see Figure 3d).³⁶

Silicomolybdate-based POMs have been used to form (POM)/metallacalixarene/graphene-based electrode materials. Two compounds were tested in a recent study, $[\text{Ag}_5(\text{C}_2\text{H}_2\text{N}_3)_6][\text{H}_5\text{SiMo}_{12}\text{O}_{40}]$ – compound 1, and $[\text{Ag}_5(\text{C}_2\text{H}_2\text{N}_3)_6][\text{H}_5\text{SiW}_{12}\text{O}_{40}]$ – compound 2, where $(\text{C}_2\text{H}_2\text{N}_3 = 1H\text{-}1,2,4\text{-triazole})$. Compound 1 performed best, with a reported capacitance of 230 F.g^{-1} at 0.5 A.g^{-1} . The materials both retained around 78.5% of their capacitance after 1000 cycles at 10 A.g^{-1} . While it is difficult to account for all the variables, in a very casual comparison between the last two cited reports,^{35,36} the metallacalixarene provided some benefit towards holding onto the POMs for longer cycle life of the as-formed electrode.

The above comparison highlights the most critical challenge faced in work where POMs are applied to SCs. That is, long term stability is highly linked to the ability to anchor POMs to a conductive framework that will exploit their redox capacity but maintain cyclability.²⁵ Progress is being made, as the metallacalixarene examples demonstrate by comparison to the AC-POM hybrid. However, when compared to commercial (AC based) supercapacitor products, where it is reasonable to see cycle ratings of over 1 million cycles with the same or greater than 75% capacitive retention and no power fade,²² it can be seen that there is still significant improvement required. The following section discusses materials that are suitable for SC electrodes, which have been synthesized with POMs, to form POM-functionalized hybrids.

2.1 POM-Functionalized Hybrids

The key opportunity that POMs offer to enhance energy storage devices lies with their ultra-dispersed nature (all or most active centers are surface atoms) and with their ability to reversibly exchange large numbers of electrons. Up to $\pm 24 \text{ e}$ per molecule has been claimed in some cases.³⁷ However, such a degree of reduction is debated and is in conflict with other knowledge on POMs, which sets a more conservative limit for the number of electrons that can be exchanged reversibly.³⁸ As a pure material, POMs are generally electrically insulating. Therefore, exploiting the desirable qualities of POM complexes requires them to be supported on conductive pathways. In the context of SC electrodes, it is of particular importance to maintain a high surface area for double layer

capacitance and high power handling, as well as chemical stability for long cycle life.³⁹ The aim of combining high surface area, electrical conductivity and chemical stability has stimulated the creation of a wide range of hybrid materials. The definition of a hybrid material herein means a POM-based material that through a given synthesis procedure has been combined at a molecular level with some other material/s to achieve synergistic properties. This section describes the hybridization of POMs with conducting polymers and various forms of nanocarbons.

The motivation for this type of best-of-both-worlds chemical hybridization is enhancing EDL performance with the redox contribution of POMs. This contribution can be quite significant. For example, the use of a polymerized imidazolium linker (PIL) cation to secure GeMo_{12} and SiMo_{12} POMs to multi-walled carbon nanotubes (MWCNTs) has been shown to achieve an increase of more than nine times the capacitive performance relative to bare MWCNTs – 191 F.cm^{-3} .⁴⁰ In this study, a layer-by-layer (LbL) method of constructing the conducting polymer-carbon-POM composite was used and was compared to using a more conventional linker, poly(dimethyl diallyl ammonium chloride) (PDDA). The performance of the PIL is significant, because PDDA as a linking polymer has itself been shown to offer reasonable performance at high charge-discharge current densities, which is synonymous with high CV scan rates. For example, PDDA-functionalized reduced graphene oxide (PDDA-rGO) was used as the conductive matrix to support $\text{PMo}_{12-x}\text{W}_x\text{O}_{40}^{3-}$ (PMoW),⁴¹ and a capacitance of 140 F.g^{-1} at 10 A.g^{-1} was reported.

Polypyrrole nanopipes (Ppy-NPipes) are another type of purely polymeric conductive framework that have been enhanced for pseudocapacitance by doping with Keggin PW_{12} and PMo_{12} type POMs.⁴² The two types of POM doped nanopipes showed elevated capacitive performance of almost 1.5 times that of the bare Ppy-NPipes with 294.1 F.g^{-1} and 341 F.g^{-1} for the molybdenum and tungsten POMs, respectively. By comparison, the bare Ppy-NPipe exhibited 204.5 F.g^{-1} . Symmetric devices using each type of POM-hybrid material exhibited high performance metrics; 6.3 and 6.8 F/cm^3 and 1.5 and 2.2 mWh/cm^3 for the molybdenum and tungsten variants, respectively.

Wide ranges of synthesis methods have been explored to produce POM hybrid electrode materials, and variations to the methods can produce interesting results. Polyaniline (PANI), one of the first discovered conducting polymers, has been combined with phosphorous, tungsten, and silicon based Keggin POMs to form molecular hybrids for supercapacitor applications.^{26,27} In one of these studies, PMo_{12} was combined with PANI and directly deposited onto current collecting foils using electrochemical deposition techniques.²⁷ The materials were deposited by two methods. An electrochemical-only method of applying a potential sweep in H_2SO_4 electrolyte (ECh) was compared to a chemical-electrochemical method (Ch-ECh). In the latter, larger amounts of precursor phosphomolybdic acid and aniline were added to the H_2SO_4 solution before the same electrochemical cycling as the former. When tested using a solid-state H_3PO_4 based electrolyte membrane in a two-cell configuration, the results showed that the ECh method outperformed the Ch-ECh approach. SEM further supported this, where, surprisingly, a much higher density of POM-PANI clusters is visible on the ECh produced electrode.

In addition to affecting the yield of materials, variation to the reaction of precursors in POM production is known to result in different stoichiometries.²¹ The Wells-Dawson 18-molybdo-2-phosphate POM, $\text{K}_6\text{P}_2\text{Mo}_{18}\text{O}_{62}\cdot 12\text{H}_2\text{O}$ (P_2Mo_{18}), has been combined with $\text{Ru}(\text{bpy})_3\text{Cl}_2\cdot 6\text{H}_2\text{O}$ ($\text{Ru}(\text{bpy})_3$) to form a molecular hybrid.⁴³ The synthesis was performed both with and without the presence of potassium iodide (KI), and this resulted in different stoichiometry for the products. The different ratio of $\text{Ru}(\text{bpy})_3$ to the linked P_2Mo_{18} molecules in turn affected the capacitance for the materials when studied for their use in neutral bio-compatible electrolyte systems. For the product formed in the presence of KI, 125 F g^{-1} was reported, versus 68 F g^{-1} for the hybrid formed without KI present. The excess of $\text{Ru}(\text{bpy})_3$ in the KI-derived material suggests that the interesting electronic properties of this ligand play an important role in the transport of charges associated with the reduction and oxidation of the POMs.⁴⁴

While the use of polymeric linkers and other ligands typically requires synthesis via carefully measured chemical reactions, simple mixing and solvo-thermal methods are facile, and therefore can

be easily adopted for other hybrid types. For example, POMs have been immobilized in Cu-based MOFs by multiple research groups, to create polyoxometalate/metal organic frameworks (POMOFs).^{45,46} *See section 3.1.1.4 for more on POMOFs in lithium batteries.* Simple one-pot mixing is also a widely applied route to synthesizing POM-nanocarbon based hybrids. Dong et al. used a Mo₁₃₂-based Kepplerate POM combined with reduced graphene oxide (rGO) and tested its performance in an asymmetric cell using modified AC as the opposite electrode.⁴⁷ However, for carbon-based materials, the interaction with POMs is relatively weak.⁴⁸ Therefore, mixing methods commonly still seek some sort functionalization of either the POM or the carbon scaffold to improve the interaction strength, albeit in reactions less sensitive to the stoichiometry. In other recent work on Keplerate POMs, Pakulski et al.⁴⁸ synthesized hybrid supercapacitor electrode material by mixing electrochemically exfoliated graphene (EEG) nanosheets with Mo₁₃₂ POM functionalized with dodecyltrimethylammonium bromide (DTAB), resulting in the formation of porous 3D superstructures. Performance in H₂SO₄ electrolyte revealed 65 F g⁻¹, 93 mFcm⁻² and 93 Fcm⁻³ respectively for the Mo₁₃₂-DTAB-EEG hybrid.

Cuentas-Gallegos et al.³¹ fabricated novel hybrid materials using Keggin type POMs and functionalized CNTs. The importance of functionalizing the CNTs is described in some detail. It enables the POMs to more securely anchor to the carbon framework during the synthesis procedure of the electrodes. The report emphasizes again the importance of ensuring strong POM-to-scaffold interactions or linking for ensuring long-term cycle stability in such hybrid materials. In another work by the same author, -NH₂ and -OH functional groups were grafted onto vulcan carbon (VC) then the material was hybridized with phosphomolybdic acid (H₃PMo₁₂O₄₀₋₁₂H₂O) to investigate its effects on capacitive performance. Functionalization and hybridization resulted in successive losses of the VC surface area. The authors propose that this is due to micropore blocking. However the -OH functionalized VC was found to improve the POM retention onto the carbon material and therefore showed better performance than other combinations studied.⁴⁹

The graphene-based material rGO is an appealing nanocarbon for hybrid electrode materials.⁵⁰

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The appeal stems from its hydrophilic nature and well-established commercial-scale production methods for its precursor, graphene oxide.^{51,52} As well, intrinsic defects in the material after reduction offer functional sites for the attachment of polar molecules. While the functional groups of rGO have been well-exploited for attaching metal-oxides for enhanced pseudocapacitance,^{53,54} research suggests that their ability to anchor POMs is less certain. In a comparative study exploring this point, phosphomolybdic acid ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$) was coupled with rGO and compared with another hybrid where the grafting of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ onto rGO sheets is aided by poly(1-vinyl-3-ethylimidazolium bromide) ([VEIM][Br]).⁵⁵ TEM of the polymer ionic liquid (IL) aided hybrid (POM/PIL/rGO) reveals individually-anchored POMs with no clumping. A maximum capacitance value of 408 F g^{-1} was recorded for the POM/PIL/rGO material, at a constant current density of 0.5 A.g^{-1} in H_2SO_4 electrolyte. This was more than two-fold higher than that of the POM/rGO material with no polymeric linker, which displayed only 162 F.g^{-1} . The POM/PIL/rGO retained 92% of its initial capacitance while the current density was increased up to 10 A.g^{-1} . In contrast, the capacitance of the POM/rGO decreased more significantly as the constant current density was increased up to the same limit, down to a value of 110 F g^{-1} . In addition, the POM/PIL/rGO material retained 98% of its capacity after 2000 cycles at 10 A g^{-1} . In other recent and notable work utilizing POM-rGO hybrids with polymeric linking, Ensafi et al. made a sponge formulated as $[(\text{n-C}_4\text{H}_9)_4\text{N}][5[\text{PW}_{11}\text{CoO}_{39}]]@ \text{IL-rGO}$. It was tested in seawater and in H_2SO_4 electrolyte. They report an impressive 834.3 F g^{-1} at a current density of 0.9 A.g^{-1} in seawater.⁵⁶ This result is promising with respect to both energy storage applications as well as capacitive deionization for water desalination.

As seen in a number of the above reports, the use of H_2SO_4 aqueous electrolyte is a popular choice for research level testing of materials and devices. In a comparative study centered on its use, $\text{PW}_{12}\text{O}_{40}$ was used to functionalize rGO, and the resulting phosphotungstate product was applied in symmetric devices. The devices were tested using $1 \text{ M H}_2\text{SO}_4$ electrolyte and examined against the same $1 \text{ M H}_2\text{SO}_4$ but with hydroquinone added for additional redox activity. The devices containing

the doped electrolyte exhibited an energy density of 2.38 Wh cm^{-3} as compared to the bare sulfuric acid system which achieved 1.05 Wh cm^{-3} .⁵⁷ This work and other similar works demonstrate the ability to boost the energy density by hybridizing the electrolyte system as well as the electrode materials.^{39,57,58} The same authors as⁵⁷ use PW_{12} and PMo_{12} again to dope rGO.⁵⁹ The materials are tested individually in symmetric cells, and then in an asymmetric device where the rGO- PW_{12} hybrid is applied as the positive electrode and the rGO- MoW_{12} is used for the negative electrode. Careful study of the redox potentials for each hybrid via CV method in two-electrode configuration prior to the assembly of the asymmetric device enabled the use of $1 \text{ M H}_2\text{SO}_4$ electrolyte in a potential window of 1.6 V , an extension of 0.3 V over the typical limit of aqueous systems.

Voltage windows have been extended even further using poly-vinyl-alcohol (PVA)/ H_2SO_4 -based gel electrolyte. A cobalt-containing Anderson-type POM was decorated on the surface of a reduced rGO aerogel via one-pot hydrothermal synthesis.⁶⁰ An asymmetric solid-state supercapacitor denoted (Co-POM/rGO// H_2SO_4 /PVA//rGO) was constructed using the gel electrolyte. The device exhibited an energy density of 37.6 Wh kg^{-1} at a power density of 500 W.kg^{-1} , with strong cycling stability, retaining 95.2% capacity after 5000 charge/discharge cycles, at a current density of 2 A g^{-1} in a 2 V window.⁶⁰ Given that the energy density of SC devices is proportional to the square of the voltage window, demonstrating good retention of capacity after thousands of cycles at 2 V represents significant advancement for devices using aqueous electrolytes.

2.2 POMs as Precursor/Template for Metal Oxides and Nitrides

Several metal oxides and metal nitrides are known as electroactive materials offering fast reversible redox activity for enhancement of electrochemical performance of electrode materials. Generally speaking, metal-oxides are limited in their conductivity,⁶¹ while metal-nitrides have limited stable voltage windows.⁶² POMs offer unique avenues to address these concerns. For instance, Dubal et al. used tungsten nitride NPs derived from PW_{12} -POM to create electrodes for asymmetric SC devices.⁶² The W_2N NPs produced from the POM precursor are used to decorate a carbon fabric (CF) that is further enhanced by phosphorous doping, where the phosphorous source is also the PW_{12} POM

precursor. An added benefit was that the negative potential window of the $W_2N@P-CF$ is larger than that of tungsten nitrides previously applied to SCs (1.2 V compared to ~ 0.8 V).^{63,64} When the $W_2N@P-CF$ negative electrode was combined with $PPy@CF$ for a positive electrode, the resulting devices were able to operate within a 1.6 V window. The process of producing the $W_2N@P-CF$ electrode material is represented schematically in Figure 4 (c). Firstly, the Keggin-type PW_{12} was anchored to the CF and subsequently carbonized in NH_3 gas to form W_2N NPs. During this process, the CF is simultaneously doped with phosphorous. The extended voltage window compared to other tungsten nitrides is also proposed to be a result of the unique synthesis. The authors state it as being due to either, or both, the effect of phosphorous doping and the ultra-small W_2N particles that are produced when using the PW_{12} POM as a precursor reagent.

The same author⁶⁵ uses PMo_{12} to generate molybdenum nitride nanocrystals while simultaneously doping a CF substrate with phosphorous to generate material denoted $MoN@P-CF$.⁶⁵ Hexagonal molybdenum nitride MXenes, a class of 2D inorganic layered materials, anchored to boron and nitrogen co-doped CNTs have also been produced using molybdenum POMs, but in this case a Lindqvist type (Mo_7O_{24}) precursor was employed.⁶⁶ These last three reports^{62,65,66} all use high temperature thermal treatment in ammonia atmosphere to achieve the nitridation of the POM-based Mo source, showing that this is an effective route to producing nanoparticle metal nitrides.

A number of Keggin-type POMs have been utilized in the synthesis of metal oxides for asymmetric SCs.⁶¹ In a single-step procedure, $KMnO_4$ was combined with PMo_{12} and treated hydrothermally to produce $\alpha-MnO_2$ “nanoflower” type product, which can be seen in Figure 5 (a-c). The hydrothermal treatment was carried out at various temperatures and for various times. PW_{12} and SiW_{12} POMs were also explored and resulted in the effective production of MnO_2 that possessed nanoparticle properties. This is an important contrast to typical metal-oxide powders that may be used for pseudocapacitive enhancement, where much larger particle sizes may be expected. In a three-electrode configuration, the PMo_{12} based MnO_2 produced at 200 °C over 24 h outperformed the other preparations, posting 235 F g⁻¹ at a current density of 0.5 A g⁻¹. When the same material was tested

in an asymmetric cell using an AC counter-electrode and neutral NaSO₄ electrolyte the cell was able to be operated in a 2 V window and retained 91% of its 45 F g⁻¹ initial (device) capacity after 5000 cycles at 3 A g⁻¹.

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The above results demonstrate that nano-sized POM particles can serve as excellent precursors to nitrides and oxides for energy storage because their high surface-to-bulk ratio enables facile and complete reactive pathways towards relevant products, and because the product materials are able to retain this property. Retaining the high surface-to-bulk means that metal oxides and nitrides produced via such routes can overcome some of the perceived limitations of conductivity and electrochemical stability, since these limitations are generally associated with the bulk properties of such materials. For example, smaller particles allow intimate contact with conductive scaffold materials. It is also proposed that smaller particles promote higher voltage windows. Therefore, producing high surface-to-bulk oxides and nitrides from POMs can effectively side-step the limitations of powdered versions of such compounds to enable end-products with desirable properties.

2.3 Roadmap to POM-based Electrolytes

The use of POMs as a component of conventional liquid electrolyte in SCs have been demonstrated but not widely explored. Skunik-Nuckowska et al.⁵⁸ used a phosphotungstate-based POM together with hydroquinone in aqueous solution as an electrolyte in a SC device where the electrodes consisted of a high performance carbon material. POMs have also been applied to other applications such as proton conducting membranes for fuel cells.⁶⁷⁻⁶⁹ These grossly different contexts for application as electrolytes show how this class of materials may have a wide range of prospects owing to its interesting physical properties.

Wu et al.⁷⁰ synthesized a phosphotungsten vanadate-based POM and investigated its properties with the view towards application as an electrolyte. The IL studied consisted of 1-(3-sulfonic group)propyl-3-methyl imidazolium cations (MIMPS) with 4PW₁₁VO₄₀ Keggin-based anions; [MIMPS]₄PW₁₁VO₄₀. Their product was a quasi-solid-state IL possessing a solid layered structure below 80 °C while transitioning to a liquid above this temperature. The electrical

conductivity of the material was measured, and the authors found a significant increase in this property above the liquid transition temperature. They report values of about $10 \times 10^{-3} \text{ S.cm}^{-1}$ at room temperature, and $8.60 \times 10^{-2} \text{ S.cm}^{-1}$ at 83°C . It was concluded that this result was due to the improved diffusion of the ions above the liquid transition temperature.⁷⁰ In a later study by Tong et al.⁷¹ results are found for two other structurally similar POM-derived ILs, $[\text{MIMPS}]_4\text{PMo}_{11}\text{VO}_{40}$ and $[\text{MIMPS}]_3\text{PW}_{11}\text{MoO}_{40}$. The same-layered structure is confirmed by XRD results, and the authors show a transition from a solid to a liquid state above around 90°C . The conductivity of these liquids was higher than that reported by Wu et al.⁷⁰ where they measured it to be 0.1 S.cm^{-1} for both $[\text{MIMPS}]_4\text{PMo}_{11}\text{VO}_{40}$ and $[\text{MIMPS}]_3\text{PW}_{11}\text{MoO}_{40}$, with electrochemical stability windows of 2 V and 4 V, respectively.

The above cases demonstrate the interesting characteristics of these novel types of electrolytes. However, the temperature ranges in which high ionic conductivity occurs make them more appropriate for application such as fuel cells etc. Charge storage devices like SCs generally require peak performance of the materials to fall in a window a few tens of degrees either side of ambient temperatures, making these gel-liquids unsuitable. Wu et al.⁷² investigated two types of IL electrolytes consisting of POM polyanions combined with tetraalkylphosphonium (TBTP) cations. They conclude that the Dawson-type POM ($\text{P}_2\text{W}_{16}\text{V}_2\text{O}_{62}$) possesses better thermal and charge conductivity properties than the Keggin-type ($\text{PW}_{10}\text{V}_2\text{O}_{40}$) to which it was compared. These conclusions are based upon the calculated energies associated with the lattice potential and the ionic migration potential, where in both cases the Dawson-type structure shows a lower energy requirement. The $[\text{TBTP}]_8 \text{P}_2\text{W}_{16}\text{V}_2\text{O}_{62}$ IL shows a phase transition from solid-gel to liquid at around 50°C which is greatly reduced against that seen in previous studies as well as against the $[\text{TBTP}]_5 \text{PW}_{10}\text{V}_2\text{O}_{40}$ Keggin-based IL against which it is compared (61°C), and almost reaching the ranges required for application in typical energy storage devices. Even though the above results lay just outside the range of practical use for energy storage, it is worth noting that the authors show a strong link between the improved properties of the Dawson type structure and its larger POM anion size.

This offers predictive insight for the rational design and selection of POM based electrolyte systems,

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which justifies further research into these ionic gel-liquid systems.

2.4 Theoretical Studies to Underpin Charge-storage in POM-Hybrids

The importance of anchoring of POMs onto a supporting scaffold has been established in previous sections. Theoretical simulations provide a powerful tool to provide insight to the binding between POMs and an associated substrate or scaffold material.

The mechanisms of bonding between carbon and POMs are not fully understood, and so to explore this further Muniz et al.⁷³ performed density functional theory (DFT) investigations into the electronic structure of a range of Keggin POMs (PdMo_{12} , RuNb_{12} , SiMo_{12} , PMo_{12} and SiW_{12}) adsorbed onto a carbon surface. These five Keggin structures were investigated for their binding lengths and electron sharing under various orientations on a carbon substrate, and neutralizing counter-ions (cations) were included to balance the charge of the Keggin anions. For PdMo_{12} and RuNb_{12} the calculation was fully predictive, as these systems have not, to date, been synthesized. For the SiW_{12} and RuNb_{12} systems, the results indicate that functionalization of the carbon surface may not be required for sufficient anchoring and feasible use as hybrid (electrode) materials.

In 2019, Dubal et al.⁶⁵ simulated the adsorption of a number of combinations of the materials used in their study of molybdenum nitride nanocrystals. Again, the simulations were performed using DFT, in this case in the Vienna Ab-initio Simulation Package (VASP). As described in detail in section 2.1, the experimental approach in this work used CF coated with PMo_{12} as a substrate. The material was then converted to MoN@P-CF , where MoN nanocrystals were formed and the CF became phosphorous doped. Simulations reveal that the phosphorous doping of the CF enhances the energy of adsorption for protons (simulated as hydronium) over the bare carbon surface. However, the MoN@P-CF material has an adsorption energy over eight times greater than that of the phosphorous-doped CF. This theoretical element of the work strongly supports the experimental findings. Likewise, Yang and co-workers⁴⁵ employed DFT calculations to explain the origin of the enhanced redox reactions in POM/PIL/RGO nanohybrids. The van der Waals density functional

(vdW-DF) for the non-local correlation part was employed in the DFT calculations. Figure 5 (d) shows the most stable POM/PIL/graphene structure, where two POMs and one IL dimer (i.e., $2[\text{H}_2\text{PMo}_{12}\text{O}_{40}][\text{C}_{14}\text{H}_{24}\text{N}_4]$) are included in a periodic unit cell. The role of PIL and the neighbouring POM in the proton transfer process was examined by calculating adsorptions energies of a single H atom on eight different O_b and O_c sites of POM (Figure 5e). These DFT results suggest that the H adsorption energetics on a POM in the POM/PIL nanohybrids is significantly affected by adjacent PILs and POMs. From an electrostatic standpoint, the PIL cations and the POM anions suppress and facilitate the proton adsorption reaction, respectively, on the adjacent POM.

Gullen et al.⁷⁴ performed in-silico simulations of the CNT functionalization that was experimentally explored by Gallegos et al.³¹ Specifically, they used DFT to investigate the bond formation between Keggin-type SiW_{12} and organic functional groups attached to a CNT. The functional groups are denoted $\phi\text{-X}$, where ϕ denotes a phenyl group and X is one of $-\text{NH}_2$, $-\text{OH}$, $-\text{COH}$, or $-\text{COOH}$. The bond lengths are similar for the different functional pairs, however $\text{SiW}_{12}@\phi-\text{COOH}/\text{CNT}$ shows enhanced attraction over the others. Whereas the first three systems explored ($-\text{NH}_2$, $-\text{OH}$, $-\text{COH}$) exhibit van der Waals type interactions, the $-\text{COOH}$ system exhibits a covalent-like binding energy, making its combinations with SiW_{12} a strong potential candidate for a stable hybrid system (Figure 5 f, g).⁷⁴

The significance of the previous study is emphasized in closing this chapter – it is well known that stabilizing POMs on a graphene surface remains challenging.⁷⁵ Therefore, predicting functional groups that are more likely to result in the successful anchoring of materials like POMs, but also other classes as well, is of great importance to rationally guide research efforts. The covalent type anchoring of POMs via carboxylate groups represents a great example of how simulation can guide novel syntheses. Therefore, combining the efforts of both theoretical work and applied materials research is an effective approach to improving devices.

3. Development of POMs for Battery Applications

The development of high-performance rechargeable batteries, including lithium-ion batteries (LIBs) and sodium ion batteries (SIBs), is one of the most important challenges in energy storage, and arguably stands to contribute as much as any other field toward solving increasing environmental and energy issues. The charge storage in rechargeable batteries results from reversible redox reactions in the electrode active materials.⁷⁶ The stored energy in batteries can be improved by either increasing the capacity of the electrode materials or exploring new cathode materials with higher voltages.⁷⁷ The following sections explore how POMs have been able to contribute to this development.

3.1 Lithium-ion Batteries

LIBs are the preferred energy storage system for many applications due to their high voltage of more than 3.5 V per cell, high energy density of up to 200 Wh.kg⁻¹ and relatively long cycle life. The most common cathode materials used in LIBs are lithium transition metal oxides including layered structures such as LiCoO₂, spinel structures such as LiMn₂O₄, or olivine structures such as LiFePO₄. However, the changes in crystal structure of these materials during the intercalation (and de-intercalation) of lithium ions result in capacity loss during cycling. Therefore, their specific capacity is usually less than 200 mAh.g⁻¹.^{76,78-80} For anodes, graphite is the most commonly used material in commercial LIBs. However, the theoretical capacity of graphite is low (372 mAh.g⁻¹), which limits its applications in large-scale systems.^{77,80} Therefore, great efforts have been dedicated to developing new materials for LIBs. Recently, POMs have received much interest as electrode materials in LIBs (Table 1). The characteristic capacity and cycling stability of POMs are independent of the material's crystalline stability because the POM molecular clusters show multi-electron redox as an individual molecule. Although POMs have low electrical conductivity, using nanosized POMs and/or mixing with conductive additives can improve their electrochemical properties.⁸¹⁻⁸⁶ Their application to LIB research can be categorized by the POM type being used, such as by the addenda atom type, or by specific groupings of hybridized materials, such as the nanocarbon or MOF hybrids described in the following sections.

3.1.1 Molybdenum-based POMs

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Phosphomolybdic acid is perhaps the most widely explored precursor to develop the electrode materials for energy storage applications. This work was pioneered in the late 90s by the group of Gomez-Romero who showed the potential of POMs in LIBs.²⁵ The group was able to demonstrate anchoring of POMs to the conducting polymer polyaniline, which allowed insertion and de-insertion of Li cations *without* simultaneously removing the POM anion.⁸⁷ This work was followed by the demonstration of the hybrid material as an electrode in LIBs.⁸⁸

Much more recently, Sonoyama and coworkers^{82,89} examined the electrochemical properties of a potassium-based variant of the Keggin-type polyoxomolybdate, $K_3[PMo_{12}O_{40}]$ (KPM), applying it as a cathode material for LIBs. The KPM showed a high initial discharge capacity over 200 mAh.g⁻¹ in the potential range of 1.5 V - 4.2 V. Although a high capacity was achieved, KPM showed poor cycle stability, as only 37.5% of its initial capacity was maintained after 50 cycles, which resulted from the structural instability of the reduced $[PMo_{12}O_{40}]^{3-}$ cluster ion in the organic solvent. Furthermore, the calculated energy density of KPM was only 480 mW.h.g⁻¹, which is not far from that of conventional cathode materials ($LiCoO_2 \sim 500$ mW.h.g⁻¹, $LiMn_2O_4 \sim 400$ mW.h.g⁻¹). This is a consequence of the lower discharge voltage of KPM (2.5 - 1.5 V) compared to the usual LIB cathode materials. Another Keggin-type POM, namely $TBA_3[PMo_{12}O_{40}]$ (TBA; $[N(CH_2CH_2CH_2CH_3)_4]^+$) was studied by Wang et al.⁹⁰ as a cathode for LIBs. The charge storage mechanism in super-reduced $[PMo_{12}O_{40}]^{27-}$ was studied by X-ray absorption near-edge structure analysis (XANES) (Figure 6 (a)). The reversible redox reaction of the 24-electrons in $[PMo_{12}O_{40}]^{3-}$ during charging/discharging process resulted in a high capacity of approximately 260 mAh.g⁻¹ at 1 mA in a voltage range of 1.5-4.2 V. Moreover, *in operando* extended X-ray absorption fine structure (EXAFS) measurements indicated that POMs behave like an electron sponge as the molecular structure size of $[PMo_{12}O_{40}]^{27-}$ shrinks when compared to the original $[PMo_{12}O_{40}]^{3-}$ (Figure 6 (b)).

The same group investigated Anderson-type polyoxomolybdate, $Na_3[AlMo_6O_{24}H_6]$ (NAM),) as LIB-cathode.⁹¹ In order to improve the low conductivity of the POMs, NAM was mixed with two

types of conductive additives, namely ketjen black (KB) and acetylene black (AB) using two different methods such as hand grinding and ball milling. Both methods and conductive additives affect the capacity and cycling stability of NAM. The maximum discharge capacity of 437 mAh.g⁻¹ was achieved, which was maintained to 399 mAh.g⁻¹ after 50 cycles for ball-milled NAM/KB sample. The above results can, at least in part be explained by: (1) the improved electric conductivity, resulting from the high electrical conductivity of the KB and producing larger contact surface area between KB and NAM through ball milling, (2) the stable structure of [AlMo₆O₂₄H₆]³⁻ during redox reaction (Figure 6c). However, the amount of NAM in the cathode was low (32 wt %), which can restrict the energy density of the cell. To further increase the discharge capacity and cycling stability, the nanosized POMs were used along with conductive additives.⁸⁴ The POM (NH₄)₆[NiMo₉O₃₂] (ANM) was investigated using either KB or AB. In this work, four different samples were tested as LIB cathode materials; ANM microparticles hand-ground with AB (m/AB), ANM NPs hand-ground with AB (n/AB), ANM NPs hand-ground with KB (n/KB), and ANM *in situ* crystallized in KB (nanocomposite ANM/KB). Better discharge capacities and cycling performance were obtained with the n/KB and nanocomposite ANM/KB. The n/KB cathode exhibited a high initial discharge capacity of 490 mAh.g⁻¹ and a very stable cycling performance, with capacity retention of 87.6% after 50 cycles. Although the nanocomposite ANM/KB cathode showed high initial capacity at low current density, it showed a poor cycling stability as compared to n/KB (61.6% after 50 cycles). This might be due to the increase in the catalytic activity of the nanocomposite ANM/KB, which leads to the formation of surface film and eventually increases its interfacial impedance. However, at high current densities (from 83 to 500 mA.g⁻¹), the nanocomposite ANM/KB showed relatively higher discharge capacity and rate-capability than that of n/KB. *Ex situ* XRD analysis indicated that the crystal structure of ANM remains amorphous during insertion and extraction of Li ions (charge/discharge processes), which enables high reversible capacity with deep discharge-charge cycles.

3.1.2 Vanadium-based POMs

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Vanadium-based POMs have proven to be practical cathode materials due to their low molecular weights leading to high specific capacities and fast charging/discharging kinetics, which resulted from their stable ionic cluster.⁹² The electrochemical properties of V-based POMs; bi-capped Keggin-type (KH)₉[PV₁₄O₄₂] (KPV),⁸⁹ K₇[NiV₁₃O₃₈] (KNiV),⁸¹ and K₇[MnV₁₃O₃₈] (KMV)⁸³, have been recently reported as LIB-cathode materials. These V-POMs displayed comparable discharge capacities to those of Mo-based POMs, but with much higher cycling performance. This indicates that the electrochemical stability of V-POM is not dependent on the stability of crystal structure, but rather on the stability of their cluster ions; [PV₁₄O₄₂]⁹⁻, [NiV₁₃O₃₈]⁷⁻ and [MnV₁₃O₃₈]⁷⁻. KPV exhibited a high initial discharge capacity of 370 mAh.g⁻¹ with cycle stability of 95% over 50 cycles, which is very high compared to that reported from KPM (~37.5%). KNiV NPs were prepared by a recrystallization method to improve the capacity and cycle performance of V-based materials. Recrystallized KNiV delivered discharge capacities of 218.2 and 121.3 mAh.g⁻¹ at current densities of 17 and 167 mA.g⁻¹, respectively. It also showed good cycling stability with a reversible capacity of about 200 mAh.g⁻¹ after 24 cycles at 17 mA.g⁻¹. The observed high capacity and rate capability most likely result from the use of nanosized KNiV, which offers improved specific surface area and reduced diffusion lengths. Concerning KMV, micro-sized KMV (m-KMV) showed a discharge capacity of 187 mAh.g⁻¹ at 17 mA.g⁻¹. When the particle size was decreased to nanoscale, discharge capacities were increased to 308 mAh.g⁻¹, for the same respective current density. However, at voltages higher than 3.8 V, nanosized KMV (n-KMV) showed overcharge capacities of 37 and 15 mAh.g⁻¹, respectively. This may result in electrolyte decomposition, which in turn leads to the formation of a thick passivating layer on the cathode. The passivation layer decreases the ionic and electronic conduction at the cathode/electrolyte interface. This is why the authors proposed to use the mixture of nano and micro-sized KMV particles (n/m-KMV; 1:1 weight ratio) (n/m-KMV). Unsurprisingly, the n/m KMV showed improved cycle performance where a high capacity retention of ~ 97% after 50 cycles at both high and low rates was achieved.

In other work, Li et al.⁹³ replaced the counter cations K^+ in $K_7[MnV_{13}O_{38}]$ (KMV) (which has large equivalent mass) by NH_4^+ with a smaller equivalent mass to fabricate $(NH_4)_7[MnV_{13}O_{38}]$ (AMV). The modified AMV nanoparticles showed a reversible capacity of 234 mAh.g^{-1} at 0.5 C , which was retained at 234 mAh.g^{-1} after 100 cycles. Moreover, AMV displayed rate capability of 53% when the C-rate was increased from 1 to 5 C . An energy density of 553 mWh.g^{-1} was estimated over 100 cycles, which was two-fold higher than that of the layered Li-transition metal oxide cathodes. To prevent the electrolyte decomposition and increase the electron transport in POMs, authors⁹⁴ coated the surface of polyoxovanadate, $K_9[PV_{14}O_{32}]$ (KPV) NPs with a conducting polymer, polypyrrole (PP) (5 nm thick). In this hybrid, a thin conducting layer provides high conductivity and avoids the irreversible reactions. The capacities of 410, 415 and 300 mAh.g^{-1} were recorded for PP-KPV at current densities of 167, 500 and 1000 mA.g^{-1} , respectively. Interestingly, PP-KPV showed a cycling stability of 90% (370 mAh.g^{-1}) and 93% (280 mAh.g^{-1}) over 50 cycles at 167 and 1000 mA.g^{-1} , respectively. This confirmed that coating PP on KPV NPs suppresses electrolyte decomposition, improves rate capability and cycling stability.

Along this line, Dong and coworkers developed a symmetrical LIBs by employing $Li_7[V_{15}O_{36}(CO_3)]$ as both cathode and anode material as shown in Figure 7 (a).⁹⁵ The reason to apply $Li_7[V_{15}O_{36}(CO_3)]$ materials as both the cathode and anode might be that the vanadium centers (V^{IV} and V^V) in the $Li_7[V_{15}O_{36}(CO_3)]$ polyanion exhibits different redox potentials (Figure 7 (b)). The symmetric cell showed a high discharge capacity of 120 mAh.g^{-1} at 100 mA.g^{-1} and long cycle life with a capacity retention of 95% after 500 cycles at 1 A.g^{-1} (Figure 7c). High energy and power densities of 125 Wh.kg^{-1} and 51.5 kW.kg^{-1} , respectively, were obtained.

Similarly, several POM-based materials were also employed as anode materials in LIBs. For instance, $Na_7H_2[PV_{14}O_{42}]$ (NPV) is an example of the V-based POM, which was illustrated by Huang et al.⁹⁶ *In operando* characterizations confirmed the continuous reduction and oxidation of vanadium during discharging/charging process, and the electron/ion sponge behavior of $[PV_{14}O_{42}]^{9-}$ where at least 30 electrons can be reversibly stored by one NPV molecule (Figure 7d). Furthermore, it was

found that NPV is an insertion-type anode rather than conversion-type anode, indicating the independence of the capacity and cycling stability from the stability and recoverability of the NPV crystal structure. As a result, a high reversible capacity of 687 mAh.g⁻¹ at 100 mA.g⁻¹ was achieved with 80% cycling stability after 150 cycles. These results confirm the ability of V-based POMs to provide better capacity and cycle stability compared to other materials, however, further studies are required to achieve practical realization.

3.1.3 POM/Carbon hybrid for LIBs

As discussed earlier, the direct utilization of pristine POMs as electrode materials in energy storage devices is limited by their poor electrical conductivity and high solubility in water and many organic solvents. Thus, it is useful to consider the use of highly conductive organic materials as substrates such as conducting polymers or carbon materials for the fabrication of POM energy storage electrodes.⁹⁷ The hybridization between POMs and nanocarbons, including carbon nanotubes (CNTs) and graphene, has been proven to increase the energy storage capability of LIBs due to the combination of the redox reaction of POMs and capacitive effect of the nanocarbons.^{86,98-101}

Different approaches have been developed to connect the POMs onto nanocarbon materials including covalent functionalization, in which POMs are covalently grafted onto organic moieties, and non-covalent functionalization using intermolecular interactions such as electrostatic interactions and the π - π interaction between POMs and organic materials.¹⁰² For instance, Kawasaki et al.⁸⁵ developed a nanohybrid POMs/SWNT system as a cathode material. They expected that the nanohybridization between the POM and SWNTs would increase the lithium ion diffusion and electron transfer through the SWNTs (Figure 8 (a)). In their study, a Keggin-type POM, TBA₃[PMo₁₂O₄₀] was deposited onto the surfaces of the SWNTs by electrostatic interactions. The nano-hybrid POM/SWNT delivered a capacity of 320 mAh.g⁻¹ with a good cycle performance. The high capacity of the POM/SWNT system can be ascribed to the high surface area and conducting super-highway of CNTs.

Several POM/CNT composites have been developed through covalent and noncovalent bonding to improve the affinity of POMs to CNTs. For example, Song et al.,⁹⁸ developed non-covalent functionalization of SWNTs with a covalently functionalized pyrene-POM hybrid (Py-SiW₁₁) and served as LIB anode. The pyrene moieties were covalently linked to the SiW₁₁ clusters to form Py-SiW₁₁ hybrids, which were then attached to SWNTs through both π - π stacking and electrostatic interactions. The SWNTs/Py-SiW₁₁ nanocomposite exhibited a capacity of 1569.8 mAh.g⁻¹ at 0.5 mA.cm⁻² and capacity retention of 37 % after 100 cycles. This work was extended by covalently grafting SiW₁₁-NH₂ onto CNTs by amide bonds to prepare CNTs/SiW₁₁ nanocomposites.⁸⁶ The covalent bonding introduces a stable link between the POMs and the CNTs and creates more sidewall defects in the CNTs, which results in more Li ion diffusion pathways. As an anode, CNTs/SiW₁₁ nanocomposite showed a capacity of 1189 mAh.g⁻¹ and capacity retention of 54.6% (650 mAh.g⁻¹) after 100 cycles. They also prepared a ternary PMO₁₂/PANI/MWNTs nanocomposite through noncovalent functionalization to further improve the connection between POMs and CNTs.⁹⁹ This was achieved by using conductive polymers, which have strong π - π interaction with CNTs and strong electrostatic interaction with POMs. The electrochemical investigation of the PMO₁₂/PANI/MWNTs nanocomposite as a LIB anode resulted in a capacity of 1572 mAh.g⁻¹, which was retained at 1000 mA.h.g⁻¹ (63.6%) after 100 cycles at 0.5 mA.cm⁻².

The capacitive effect of POM/nanocarbon composites can be further improved by using graphene, which has higher available specific surface area than CNTs. Hence, several studies regarding POM/graphene nanocomposites have been reported for capacitive-type devices.^{39,50,57} These types of composites are also appealing for battery applications, for example, Wang et al.¹⁰⁰ reported a Keggin-type SiW₁₂/rGO nanocomposite as a cathode material for LIBs. A capacity of 275 mAh.g⁻¹ was achieved at a current density of 50 mA.g⁻¹, which was $\sim$ 1.7 times higher than that of the pure SiW₁₂ (160 mAh.g⁻¹). Kume et al.¹⁰³ developed TBA₃[PMo₁₂O₄₀]/rGO hybrid as LIB cathode material by grafting POM molecules onto the surface of rGO (Figure 8 b, c), demonstrating a capacity of $\sim$ 140 mAh.g⁻¹ with a stable capacity over 10 cycles. Likewise, Xie et al.¹⁰¹ prepared

ethylenediamine-functionalized rGO (EDAG)/Anderson-type $\text{Na}_3[\text{AlMo}_6\text{O}_{24}\text{H}_6]$ (NAM) composite and tested as anode in LIBs. The material showed a discharge capacity of 1835 mAh.g^{-1} at 100 mA.g^{-1} .

Further work to improve the capacity and cycling stability of POM/graphene nanocomposites was performed by Ni et al.¹⁰⁴ A 3D graphene/polyaniline/POM hybrid (rGO@PANI/PW_{12}) was developed as LIB-cathode, which showed a specific capacity of 285 mAh.g^{-1} at 50 mA.g^{-1} with good rate capability (140 mAh.g^{-1} at 2 A.g^{-1}) and excellent cycling stability (only 0.028% loss per cycle capacity) over 1,000 cycles. The high capacity and good cycle stability of the reported (rGO@PANI/PW_{12}) cathode can be attributed to the fast electron transfer from reduced PANI polycation to PW_{12} polyanion, as well as the high redox properties of the PW_{12} . Nevertheless, deeper insight and understanding into the nature of the charge transfer between the POMs and the conducting supports is required in order to realize their practical application in LIBs.

3.1.4 POMs/Metal-Organic Frameworks (POMOFs)

Metal-Organic Frameworks (MOFs) is a new class of porous materials, which has attracted tremendous attention due to their unique surface and structural properties. Recently, MOFs are also investigated as host to immobilize POMs to prevent their solubility in organic electrolytes.¹⁰⁵⁻¹¹¹ The combination of POM and MOFs is hereafter referred as POMOFs. The unique combination of features of both POMs and MOFs such as open porous structures and redox-rich chemistry makes them potential materials for LIBs. Recently, Yue et al.¹¹⁰ designed a POMOF, which consists of (Ni_6PW_6) structural building units and rigid carboxylate linkers. When applied as anode in LIBs, this POMOF showed a discharge capacity of 1421 mAh.g^{-1} at 1.25 C with a reversible capacity of about 350 mAh.g^{-1} after 500 cycles. At low C-rate of 0.25 C, a high discharge capacity of 1525 mAh.g^{-1} was measured, which was retained to 540 mAh.g^{-1} after 360 cycles. Huang et al.¹⁰⁵ synthesized crystalline POMOF with an ultra-stable structure by connecting $\text{Zn-}\epsilon$ -keggin, [ϵ - $\text{PMo}_8\text{Mo}_4^{\text{VI}}\text{O}_{37}(\text{OH})_3\text{Zn}_4$] with TPT ligands, (TPT=tris-(4-pyridyl)triazine) to fabricate [$\text{PMo}_8\text{Mo}_4^{\text{VI}}\text{O}_{37}(\text{OH})_3\text{Zn}_4$][TPT]₅·2TPT·2H₂O (NNU-11) with π - π stacking interactions. The material was further tested as anode material in LIB, which showed a capacity of $1322.3 \text{ mAh.g}^{-1}$

with a stable reversible capacity of 750 mAh.g⁻¹ over 200 cycles. The authors also synthesized two thermally-stable POMOFs with diamond topology, (TBA)₃[PMo₈^VMo₄^{VI} O₃₈(OH)₂Zn₄(IN)₂] (NENU-506) and (TBA)₃[PMo₈^VMo₄^{VI} O₃₈(OH)₂Zn₄(PBA)₂]·H₂O (NENU-507) (where IN = isonicotinic acid, TBA = tetrabutylammonium ion, H PBA = 4-(pyridin-4-yl) benzoic acid).¹⁰⁷ When these two POMOFs were used as anode materials, the better cycling stability was obtained for NENU-507, which delivered a reversible capacity of 640 mAh.g⁻¹ at 100 mA.g⁻¹.

Several studies have been conducted by Lan's group in order to improve the electronic conductivity of POMOFs. For instance, they reported on POMOF-based PMo₁₀V₂/rGO nanocomposites as LIB-anode. The composite exhibited a reversible capacity of 1075 mAh.g⁻¹ at 50 mA.g⁻¹ and cycling stability of nearly 100% at both 2000 and 3000 mA.g⁻¹ current densities after 400 cycles.¹⁰⁸ They also used ILs to increase the conductivity of POMOFs by encapsulating ILs into POMOFs and fabricate a series of POMs-ILs@MOFs crystals.¹¹¹ Among those, PMo₁₀ V₂-ILs@MIL-100 crystals showed an excellent cycling stability with a high capacity of 1248 mAh.g⁻¹ at 0.1 A.g⁻¹ after 100 cycles as LIB-anode material. Likewise, Li et al.¹⁰⁶ reported POMOF (CuPW)/SWNTs composites, (CuPW=([Cu₁₈(trz)₁₂ Cl₃(H₂O)₂][PW₁₂O₄₀]) as anode materials where SWNTs were utilized as a conductive scaffold. The material showed a reversible capacity of 885 mAh.g⁻¹ after 170 cycles at 100 mA.g⁻¹. The high capacity and reasonable rate performance can be ascribed to the high specific surface area and the improved electric conductivity due to SWNTs.

From the above results, it is apparent that the POMOF/conductive composites have great potential to achieve high capacity and good cycle stability for LIBs applications. However, the complicated synthesis methods and the difficulty of anchoring the charge-balanced POMOFs on the negatively charged carbon supports limit their practical applications. Therefore, finding new simple synthesis methods to improve the conductivity of POMFs is highly demanded.

3.2 Sodium-ion Batteries

Sodium-ion batteries (SIBs) are a promising technology for large-scale energy storage applications due to the large abundance of sodium in the Earth-crust (23 × 10³ ppm) and it also permits

the use of low-cost aluminum as a current collector for both anode and cathode materials. The latter is possible because sodium does not alloy with aluminum, unlike lithium.¹¹²⁻¹¹⁴ However, their energy density is low compared to LIBs because of the large radius of the Na⁺ ions (Na⁺: 1.02 Å vs Li⁺: 0.67 Å), large atomic weight (Na: 23 vs Li: 7) and low operating potential (Na: 2.71 V vs Li: 3.04 V).¹¹⁴ Therefore, many studies have aimed to overcome these disadvantages by exploring and developing new cathode materials. Although POMs have been widely used in both cathodes and anodes in LIBs with good capacity and cycling stability, few studies have been conducted on POM-based SIBs. For instance, Liu et al.¹¹³ reported on Na₂H₈[MnV₁₃O₃₈] (NMV) as a SIB cathode material by coating NMV nanoplates on graphene sheets to fabricate a robust NMV/G composite. *Ex-situ* X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared (FT-IR) spectroscopy analyses showed that the NMV cathode acts as an electron/Na⁺ ion sponge, in which [MnV₁₃O₃₈]⁹⁻ is reduced to [MnV₁₃O₃₈]²⁰⁻ by storing 11 electrons with an expansion in size of ~7.5% (Figure 9). The NMV/G composite demonstrated a high reversible capacity of ~190 mAh.g⁻¹ at 0.1 C with good rate capability (130 m.h.g⁻¹ at 1 C), and capacity retention of 81% (140 mAh.g⁻¹) after 100 cycles. Similarly, Chen et al.⁹⁵ used Li₇[V₁₅O₃₆(CO₃)] as a high capacity cathode material for SIBs. According to electrochemical investigations and DFT, (V₁₅O₃₆(CO₃)) can transport and store large numbers of large cations such as Na⁺. A reversible specific capacity of 240 mAh.g⁻¹ was obtained at a current density of 50 mA.g⁻¹ and a stable reversible capacity of 190 mAh.g⁻¹ was retained after 30 cycles at 100 mA.g⁻¹.

The vanadium-based POM, Na₆[V₁₀O₂₈]·16H₂O, has been reported by Hartung et al. as an anode material for SIBs.¹¹² Na⁺ is (de)inserted (from) into the space between the individual [V₁₀O₂₈]⁶⁻ clusters instead of intercalating into their crystal structures, which resulted in the capacity of ~276 mAh.g⁻¹ at 20 mA.g⁻¹. Xie and coworkers¹⁰¹ employed NAM-EDAG (NAM: Anderson-type Na₃[AlMo₆O₂₄H₆], EDAG: ethylenediamine-functionalized rGO) as anode for SIB and found a reversible Na storage capacities of ~150 and ~50 mAh.g⁻¹ after 150 and 200 cycles, respectively. However, these values are much lower than those previously reported for LIBs (> 1000 mAh.g⁻¹ after

100 cycles). These low capacities can be related to sluggish electrode kinetics due to the formation of a Na₂O passivation layer during the first charging/discharging cycles; however, future research is needed to validate this conclusion. Another SIB anode material based on POMs, Na₇[H₂PV₁₄O₄₂]·nH₂O (NPV) (n=15-24), was reported by Lin et al.¹¹⁵ This anode showed a high reversible capacity of 322 mAh.g⁻¹ at 25 mA.g⁻¹ and high cycling stability 87% after 120 cycles.

3.3 POM-based Redox Flow Batteries

Redox flow batteries (RFBs) are an emerging technology for stationary energy storage. Unlike conventional secondary batteries they utilize liquid electrodes.^{116,117} RFBs use two redox-active solutions with different redox potentials, known as an anolyte and catholyte. The two solutions are stored in separate containers and are continuously pumped through battery stack compartments where reversible redox reactions can occur at the interface of each inert electrode.¹¹⁸ The anolyte and catholyte solutions are separated by an ionic conducting membrane or separator, which allows the transport of charge carrying ions. A schematic diagram of a RFB is shown in Figure 10. The unique design and the working mechanism of the RFB offers several promising features. As an example, their flexible modular design allows RFBs to be sized, as required, to cover a wide range of energy and power requirements of the consumer market. The energy and power characteristics of RFBs are not as explicitly coupled with each other when compared to other classes of batteries. This is due to the electrolyte and electrode being stored in separate containers. The de-coupling of these characteristics makes them unique for commercial application.¹¹⁷ In case of RFBs, the energy capacity is related to the volume of the electrolyte reservoirs, while the power capability depends upon the size of the battery stack. These highly customizable features of RFBs make them one of the most promising technologies for stationary energy storage.

In 1970, the National Aeronautics and Space Administration (NASA) proposed the concept of RFBs for the first time, using the ferric/ferrous and chromic/chromous as an electrolyte solution. However, the limited cycling stability and the excessive hydrogen generation at the negative electrode limited the use of ferric/ferrous and chromic/chromous as practical electrolyte solutions for RFBs.¹¹⁹

To enhance the energy density and achieve good cycling stability, various redox active species have been investigated.¹²⁰ On the basis of classification by active redox species, these RFBs can be divided as follows: all-vanadium, polysulphide/bromine, zinc/bromine, vanadium/cerium.^{121,122} Each flow battery system has certain advantages and disadvantages. Recently, POMs have been also studied in RFBs to enhance their electrochemical parameters. Pratt et al.¹²³ developed RFBs by using the phosphorus-based POMs ($A-\alpha-PV_3W_9O_{40}^{6-}$, $B-\alpha-PV_3W_9O_{40}^{6-}$, and $P_2V_3W_{15}O_{62}^{9-}$). The electrochemical measurements show that the vanadium centers of these compounds could be used as the positive electrode ($PV^{IV}_3W^{VI}_9O_{40}^{9-}/PV^V_3W^{VI}_9O_{40}^{6-}$) and that the tungsten centers could be used as the negative electrode ($PV^{IV}_3W^{VI}_9O_{40}^{9-}/PV^{IV}_3W^V_3W^{VI}_6O_{40}^{12-}$). Similarly, $[SiV^V_3W^{VI}_9O_{40}]^{7-}/[SiV^{IV}_3W^{VI}_9O_{40}]^{10-}$ could be used at the positive electrode and $[SiV^{IV}_3W^{VI}_9O_{40}]^{10-}/[SiV^{IV}_3W^V_3W^{VI}_6O_{40}]^{13-}$ at the negative electrode, $[(SiFe_3W_9(OH)_3O_{34})_2(OH)_3]^{11-}/[(SiFe_3W_9(OH)_3O_{34})_2(OH)_3]^{14-}$ at the positive electrode and $[(SiFe_3W_9(OH)_3O_{34})_2(OH)_3]^{17-}/[(SiFe_3W_9(OH)_3O_{34})_2(OH)_3]^{14-}$ at the negative electrode for the RFBs.^{124,125} However, the low coulombic efficiency and the poor cycling stability of the POM-based anolyte and catholyte solutions are challenges that still need to be addressed to make them suitable as candidates for RFB applications. Not surprisingly, the hybridization of POMs with another conducting material has recently been proposed to enhance the electrochemical performance of POM-based RFBs.^{126,127} Dubal et al. proposed the hybridization of graphene and POMs (phosphomolybdate and phosphotungstate) for flow energy storage application.¹²⁷ The distinctive feature of this work was the use of the customized hybrid electrolyte in a proprietary miniature flow reactor to study the electrochemical features. Remarkably, rGO/phosphomolybdate based flow cells showed encouraging electrochemical features including specific capacitance of 305 F.g⁻¹ with cycling stability (~95%) as well as a strong Coulombic efficiency (~77–79%) after 2000 cycles. The electrochemical results obtained for these POM based RFBs are still far from the vanadium RFBs.¹²⁸ Therefore, more efforts and new approaches are necessary to utilize POMs as liquid electrodes in RFBs.

4. Engineering of POM-based Materials for Catalysis

The Keggin types of POM are best suited for catalysis application as they are uniquely stable amongst other structural motifs. As a result, they have already been applied in various industrial processes as a catalyst.¹²⁹ They owe their extraordinary catalytic properties to the presence of numerous active sites per molecule. Their proton binding sites promote acid-catalyzed reactions and their electron-rich oxygen sites promote base-catalyzed reactions. However, the most important active sites in POM/heteropolyacid (HPA) compounds are at metal atoms, which take part in all oxidative reactions, some acid-catalyzed reactions, and other reactions. The precise active sites of POMs depend upon the type of reaction. As a catalyst used in oxidative reactions, POM/HPA (mostly W/Mo-based) compounds are well explored. In the case of substituted W/Mo, the active sites depend upon the type of metal ion substituted. Considering the variety of the metals that can be introduced into POMs, these active sites can be engineered to tailor their properties for specific applications.

In recent years, research on materials for clean and sustainable energy sources has grown substantially. Splitting water to produce hydrogen and oxygen is one convenient way for energy conversion.¹³⁰ Due to their stability and extensive tunability, POMs are attractive as water reduction catalysts for the hydrogen evolution reaction (HER), and most expansively, water oxidation catalysts (WOCs) for the oxygen evolution reaction (OER).¹³¹⁻¹³³ Indeed, POMs have been successfully implemented in the fabrication of overall water splitting systems.¹³⁴ On the other hand, electrochemical oxygen redox reactions are considered to be the key for energy conversion and storage including fuel cells and metal–air batteries.¹³⁵ In general, fuel cells devices are based on the electrocatalytic oxidation of a fuel (e.g. hydrogen and methanol) at the anode and the oxygen reduction reaction (ORR) at the cathode. Notably, OER (section 4.1) and ORR (section 4.2) are the two fundamental reactions in fuel cells and energy storage devices. In ORR, strong double bonds have to be broken for the formation of hydroxyl or peroxide ions from oxygen molecule and vice versa is true for OER, both reactions involving four electrons. Hence, they are often described as sluggish compared to their anodic counterparts, namely hydrogen evolution and oxidation which are

two electron processes.¹³⁶ Therefore, it is necessary that the catalysts used for ORR and OER are highly active for achieving better performance parameters of the devices, which has stimulated the development of novel water oxidation and oxygen reduction catalysts over the past years. Furthermore, the fascinating properties of POMs, including tunable acidity and redox properties, have stimulated the research in a wide range of POM-catalyzed applications¹³⁷ including other catalytic reactions such as CO₂ reduction, N₂ reduction and biomass conversion (section 4.3).

4.1 Water Oxidation

Water oxidation involves the dissociation of protons and electrons from stable water molecules, as well as the formation of an O–O bond from formally separated water molecules. The overall OER process typically occurs via four elementary steps involving different reaction intermediates and the formation of an O–O bond (eventually released as O₂). This latter step has been proposed to occur through two primary pathways, the water nucleophilic attack (WNA) and the interaction of two metal-oxo entities (I2M).¹³⁸ As shown in Figure 11, both reaction paths begin with two proton electron transfer (PET) events, giving rise to a metal-oxo intermediate. The WNA mechanism involves the nucleophilic attack of a solvent water molecule together with a PET resulting in a hydroper-oxo intermediate, which finally evolves molecular oxygen via another PET. On the other hand, the O–O bond formation in the I2M mechanism involves the coupling of two separate metal-oxo moieties, leading to a peroxo species that eventually produces O₂ and regenerates the catalyst. In addition to the intrinsic thermodynamic demands of water splitting, kinetic obstacles impose significant activation energies (overpotentials) and require the development of efficient catalysts.¹²⁹ WOCs composed of all-inorganic POMs have advanced the field of water splitting over the past decade.¹³¹ Lacunary POMs, “defect” structures made by removing M=O entities, are good inorganic multidentate ligands to stabilize multi-metal oxide clusters. Thus, the robust structure of lacunary POM ligands have been exploited for the assembly of catalytically active transition metal-oxo clusters. Herein, in the following section we discuss the progress on POM WOCs organized in terms of the transition metal providing the active sites in the catalyst. Comparison of the catalytic

activity of different systems is only possible in the case of uniform experimental conditions for all water oxidation catalytic species. However, since not all systems can perform under the same combination of conditions, comparison of different catalysts should be done with caution. As discussed by Hill et al,^{133,139} there have not been any established agreements on how to compare catalyst's activity of different systems in the literature. Nevertheless, in the following section catalysts will be often compared in terms of turnover numbers (TON: ratio of product formed per catalyst molecule) and turnover frequencies (TOF: d(TON)/dt) under analogous experimental conditions.

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4.1.1 Ruthenium-based POM WOCs

Ru-based catalysts are interesting because of their ability to act as a powerful oxidant in near-neutral pH conditions. In 2008, Bonchio¹⁴⁰ and Hill¹⁴¹ groups simultaneously reported $[\text{Ru}_4\text{O}_4(\text{OH})_2(\text{H}_2\text{O})_4(\text{SiW}_{10}\text{O}_{36})_2]^{10-}$ (Ru_4Si_2) as a highly-active WOC using strong oxidants. The structure of Ru_4Si_2 consists of a tetra-nuclear Ru(IV) aqua-ion, $[\text{Ru}_4(\text{O})_4(\text{OH})_2(\text{H}_2\text{O})_4]^{6+}$, entrapped by the assembly of two keggling-type lacunary $[\text{SiW}_{10}\text{O}_{36}]^{8-}$ POM units (Figure 12a). The active site of the compound is the $[\text{Ru}_4\text{O}_4]$ core with adjacently coordinated aqua ligands, which undergo four consecutive oxidation steps, from Ru^{IV}_4 to Ru^{V}_4 , followed by nucleophilic attack and water oxidation.¹⁴²⁻¹⁴⁵

In 2009, Geletii et al. studied Ru_4Si_2 as an efficient homogeneous WOC at neutral pH for visible-light-driven water oxidation.¹⁴⁶ This well-established technique is based on the facile generation of the oxidant $\text{Ru}(\text{bpy})_3^{3+}$ by photoinduced electron transfer between the photosensitizer (PS) (e.g., $\text{Ru}(\text{bpy})_3^{2+}$) and an appropriate sacrificial electron acceptor (SA) (e.g., $\text{S}_2\text{O}_8^{2-}$). Under the experimental conditions described in Figure 12 b, the Ru_4Si_2 catalyst showed high TON of up to 180, as well as initial TOF of up to 0.08 s^{-1} and the overall quantum yield (Φ : moles of generated product/moles of absorbed photons) as high as 4.5%. Later, the congeneric POM catalyst $[\text{Ru}_4(\text{O})_5(\text{OH})(\text{H}_2\text{O})_4(\text{PW}_{10}\text{O}_{36})_2]^{9-}$ Ru_4P_2 was synthesized and shown to be a WOC, although it was somewhat less efficient (lower O_2 yields under similar photochemical conditions).¹⁴⁷

Hole scavenging ability is a key parameter in the electron-transfer (ET) rate between the photogenerated oxidant $\text{Ru}(\text{bpy})_3^{3+}$ and the catalyst Ru_4Si_2 , leading to O_2 evolution. The catalyst must be able to scavenge the holes in $\text{Ru}(\text{bpy})_3^{3+}$ in competition with charge recombination. In an effort to shed light on hole scavenging, Orlandi et al. performed a nanosecond laser flash photolysis investigation on the hole transfer reaction from photogenerated oxidant $\text{Ru}(\text{bpy})_3^{3+}$ complexes to catalyst Ru_4Si_2 .¹⁴⁸ The oxidant species generated by oxidative quenching with a SA in homogeneous solution showed very fast hole scavenging from photogenerated Ru^{III} species to Ru_4Si_2 . However, at high catalyst concentrations, the electrostatic interaction between the PS, $\text{Ru}(\text{bpy})_3^{2+}$, and Ru_4Si_2 leads to efficient static quenching of the $\text{Ru}(\text{bpy})_3^{2+}$ excited state.¹⁴⁹ This energy wasting process is detrimental to photocatalytic activity, as it competes appreciably with the primary photoreaction of the excited PS with the SA, even in high ionic strength media. In this context, keeping the catalyst concentration as low as possible can prevent quenching of excited $\text{Ru}(\text{bpy})_3^{2+}$, however, at the cost of slowing the hole-transfer process. Another strategy to overcome this issue is the use of PSs that favor the productive, reductive quenching of the excited PS by Ru_4Si_2 rather than the unproductive oxidative quenching. This implies the use of PSs being strong electron acceptors in the excited state, such as a tetranuclear dendrimeric Ru^{II} polypyridine complex^{150,151} or multi-perylene-bisimide chromophores.¹⁵²

In the common oxidative quenching pathway in the presence of an SA, oxidized PS is irreversibly produced so that, in principle, fast hole transfer is not a strict requirement. In practice, however, the PSs, in their oxidized form, are often unstable under the reaction conditions used and fast hole scavenging is pivotal to minimize their decomposition (usually the main limiting factor in terms of turnover performance). As electron transfer from catalyst to PS is primarily diffusion controlled, PS degradation can be mitigated on a photoelectrode, where a close contact exists between the two components and transfer of electrons from the catalyst occurs rapidly after oxidation of the PS.¹⁴⁸ Several triadic photoanodes composed of nanoporous MO_2 ($\text{M} = \text{Ti}, \text{Zr}$ and Sn) films sensitized with different cationic Ru PSs have been reported.¹⁵³⁻¹⁵⁵ The surface-bound cation electrostatically

interacts with negatively charged Ru_4Si_2 . In the presence of Ru_4Si_2 , the electron transfer from the PS to MO_2 was found to be the main pathway, with ultrafast (nanosecond) electron transfer from Ru_4Si_2 to the oxidized PS. The oxidized catalyst is long-lived and thus, it energetically reacts with H_2O to produce O_2 . When using 3-aminopropyltriethoxysilane (APS) in particular, amine groups can be readily displayed on photoelectrode surfaces by its hydrolytic condensation and used to immobilize Ru_4Si_2 electrostatically, the very high charge of Ru_4Si_2 (10^-) render these catalyst–surface linkages very robust. Hill's group reported that Ru_4Si_2 and Ru_4P_2 can be electrostatically adsorbed on TiO_2 ¹⁵⁶ or Fe_2O_3 ¹⁵⁷ photoanodes after modification with APS. Under ultraviolet (UV) illumination, photoelectrochemical measurements indicated an enhanced photocurrent compared to unfunctionalized photoanodes. Moreover, atomic layer deposition was successfully used to protect the attachment of POM WOCs on the surface of visible-light-absorbing hematite (Fe_2O_3) photoanodes.¹⁵⁷ Instead of immobilization within a host material with a well-defined porous structure, it is also possible to immobilize catalysts by *in situ* hybridization with polymeric materials on the surface of photoelectrodes. Very recently, Ru_4Si_2 was co-deposited on WO_3 photoanodes with various electropolymerized conducting polymers.¹⁵⁸ The photoelectrochemical performance for visible-light-driven water oxidation of WO_3 photoanodes can be remarkably improved only when co-depositing polypyrrole (PPy) and Ru_4Si_2 due to the desired energy level alignment for efficient charge transfer.

Electrochemical water oxidation has been demonstrated using Ru_4Si_2 . In 2010, Toma et al. reported the effective anchoring of Ru_4Si_2 onto a conductive bed of MWCNTs as the conductive substrate to form an active water oxidation electrocatalyst (Figure 13).¹⁵⁹ Compared to amorphous carbon functionalized with Ru_4Si_2 , the electrocatalytic activity of Ru_4Si_2 on the derivatized MWCNTs was significantly higher, presumably due to the enhanced electron transfer events in the MWCNTs. The TOF of 300 h^{-1} at an overpotential of (η) 0.60 V , exceeds the values reported previously for Co-oxide and Mn-cluster systems, which were in the range $0.7 - 20 \text{ h}^{-1}$ at $\eta \geq 0.40 \text{ V}$.^{160,161} Similarly, covalent and noncovalent approaches to functionalize CNTs with cations have been explored.¹⁶²

An improvement of the electrocatalytic performance of Ru₄Si₂ is conferred by using graphene covalently functionalized with organic hydrogen-bonding cations.¹⁶³ This hybrid material catalyzes oxygen evolution at a η as low as 0.3 V at neutral pH with negligible loss of performance after 4 h of testing, outperforming the catalytic efficiency of the isolated Ru₄Si₂ by one order of magnitude, with a two-fold enhancement compared to the nanotube analogs. Based on the observation that graphene without a modified surface can adsorb Ru₄Si₂ strongly, Ru₄Si₂ was immobilized electrostatically onto graphene electrochemically deposited on a glassy carbon or indium tin oxide (ITO) electrode.¹⁶⁴ The composite material showed excellent catalytic activity and high stability under neutral pH conditions with a moderate η of 0.35 V. Moreover, Ru₄Si₂ on graphene displayed higher catalytic activity compared to RuO₂ on graphene, where the amount of RuO₂ would be ~200 times more than the amount possible from complete decomposition of Ru₄Si₂.

Another surface entrapment technique to fabricate catalytic electrodes consists of the employment of a conducting polypyrrole matrix and the layer-by-layer (LbL) technique. Ru₄Si₂ was successfully immobilized onto polypyrrole-modified glassy carbon and ITO surfaces by alternate deposition of anionic Ru₄Si₂ and a Ru(II)-metallodendrimer as the cationic moiety.¹⁶⁵ The Ru₄Si₂-based LbL assemblies exhibited enhanced electrocatalytic abilities in pH-7, in comparison to both Ru₄Si₂ paste electrodes and LbL assemblies composed of the Ru-free parent POM moiety. Apart from Ru₄Si₂ and its analogous Ru₄P₂, other Ru-based POM WOCs have also been reported. In 2011, Murakami et al. synthesized and characterized two mononuclear complexes [Ru^{III}(H₂O)SiW₁₁O₃₉]⁵⁻ and [Ru^{III}(H₂O)GeW₁₁O₃₉]⁵⁻ for water oxidation with the strong oxidant (NH₄)₂[Ce^{IV}(NO₃)₆].¹⁶⁶ Maximum TONs of up to 20 and 50 were reported, respectively. These catalysts turned to be less robust than Ru₄Si₂, despite the exposed and accessible metal center. DFT calculations indicate that the Ru^{III}-H₂O center can accommodate a stepwise multi-electron redox processes at the high reduction potential condition of Ce^{IV}/Ce^{III} to achieve the active group [Ru^V=O], and the high valent oxo-Ru^V species are responsible for the O-O bond formation event.¹⁶⁷ The calculated results support that the bridging O atom of the POM ligand will act as the most favorable proton acceptor in the O-

O bond formation, with an energy barrier of 28.43 kcal.mol⁻¹. Car et al. synthesized a triruthenium-substituted POM, [(Ru₃O₃(H₂O)Cl₂)(SiW₉O₃₄)]⁷⁻, that features a capping (Ru₃) unit connected to a lacunary [SiW₉O₃₄]¹⁰⁻ POM shell via Ru–O.¹⁶⁸ The maximum TON (23) under photocatalytic conditions was reached after 120 min, with higher TOF (0.7 s⁻¹) than the previous results for Ru–POMs. The WOC activity was derived from the formation of a recyclable POM–photosensitizer complex in the initial stages of the reaction that hinders POM decomposition into RuO_x catalysts.

4.1.2 Cobalt-based POM WOCs

The current approach for the development of more sustainable catalysis is the use of metals with high crustal abundance. In this context, the discovery of the first Co-based POM WOC represented a great breakthrough in the field given its higher abundance than Ru. For example, reported in 2010 by Yin et al., [Co₄(H₂O)₂(PW₉O₃₄)₂]¹⁰⁻ (Co₄P₂), a tetra-cobalt complex protected by two [PW₉O₃₄]⁹⁻ ligands, showed water oxidation activity with TONs reaching ~ 10³ in under 3 min in the presence of the chemical oxidant [Ru(bpy)₃]³⁺ at pH 8.¹⁶⁹ In later studies, Co₄P₂ activity was noted and studied for light-driven water oxidation using Ru(bpy)₃²⁺ as the PS and S₂O₈²⁻ as the SA.¹⁷⁰ Co₄P₂ showed remarkably superior photocatalytic performance to that of the Ru₄Si₂ catalyst,¹⁴⁶ with a TOF of ≈5 s⁻¹, Φ of 30% and a TON > 220. Co₄P₂ enwrapped into ordered mesoporous carbon nitride (MCN) exhibited noticeable electrocatalytic activity in water oxidation.¹⁷¹ At 1.4 V vs Ag/AgCl, the TOF reaches up to 0.3 s⁻¹ at pH 7, which is nearly 6 times higher than that with Ru₄Si₂@MWCNTs (0.055 s⁻¹ at 1.4 V).¹⁵⁹

The activity of Co₄P₂ as a homogeneous WOC is subject to some debate. For instance, Finke's group first demonstrated that under electrocatalytic conditions, Co^{II} leaching from Co₄P₂ can deposit onto the anode as cobalt oxide (CoO_x) film that rapidly becomes the major catalyst.¹⁷² Since then, the integrity of Co₄P₂ has been carefully examined through a plethora of studies,¹⁷³⁻¹⁷⁷ leading to the conclusion that the specific conditions such as buffer, pH, and catalyst concentration matter greatly in determining the true WOC. Ultimately, Hill's group demonstrated that Co₄P₂ is indeed the main WOC under the homogeneous conditions reported originally.¹⁷⁸ The authors described a new protocol

for the extraction of highly negatively charged POM WOCs using heptylammonium nitrate (THpANO₃) dissolved in toluene to identify the active species for water oxidation. In the end, Co₄P₂ has become a prime example for stability analysis of POM WOC systems and studies aiming to identify the main active species. Indeed, the atomic structures of POMs are highly amendable under different conditions of pH, applied potential and chemical environments, leading to ambiguity when interpreting the catalytic behaviours of OER studies.^{179,170, 169} Very recently, Folkman et al. reported phosphorous-31 nuclear magnetic resonance (NMR) and cathodic stripping analysis to determine the amount of detectable Co^{II}(aq) in solutions of a series of six exemplary Co-POMs (including Co₄P₂^{180,181}). Higher pH values and phosphate buffer in general led to higher levels of Co^{II}(aq). However, under pH 5.8 the Co-POMs exhibited higher stability, where the amount of Co^{II}(aq) detected cannot account for the observed electrochemical water oxidation activity. It seems that the specific conditions are important in determining the identity of the dominant WOC. This study exemplifies a valuable methodology for distinguishing between homogeneous and heterogeneous WOCs derived from Co-POMs, even when metal-leaching is present at just micromolar levels. Furthermore, under the umbrella of WOC optimization, advanced *in situ*/operando analytical techniques (such as X-ray absorption spectroscopy, XPS, X-ray scattering techniques among others) are being developed as increasingly powerful tools to elucidate the controversial discussions about the molecular or nanoscale nature of many POM WOCs. More and more of these approaches also enable the monitoring of possible key intermediates as an essential prerequisite for proposing catalytic mechanisms. An overview of emerging *in situ*/operando approaches as new strategies for monitoring WOC transformations has been published recently.¹⁸¹

Recent advances in heterogenizing POMs on electrode surfaces provide protocols and criteria to assess the stability, rates, and molecular nature of immobilized WOCs. For example, MOFs have been used to encapsulate Co₄P₂ displaying enhanced photocatalytic and electrocatalytic water oxidation activity as well as improved stability facilitated by the electrostatic interaction with the MOF.¹⁸² Recently, Co₄P₂ has been immobilized in the hexagonal channels of a porphyrinic MOF

(MOF-545) hybrid framework (Figure 14a),¹⁸³ with the catalyst and the PS (porphyrin linker) within the same porous solid material. As shown in Figure 14b, O₂ was formed immediately upon exposure to light and increased linearly with time, exhibiting high photocatalytic activity (TOF = $40 \times 10^{-3} \text{ s}^{-1}$ for the first 15 min and TON of 70), good stability and easy recyclability.

It is also possible to immobilize Co₄P₂ by *in situ* hybridization with polymeric materials on the surface of photoelectrodes. Recently, a synthetic melanin thin film incorporating Co₄P₂ was readily deposited on the surface of various n-type inorganic semiconductors (e.g., Fe₂O₃, BiVO₄, and TiO₂) by electropolymerization.¹⁸⁴ The formation of a melanin-based p–n heterojunction structure results in an increased photocurrent density and decreased onset potential for water oxidation when compared to the bare semiconductor photoanodes. In a different approach, electrostatic, non-covalent immobilization strategies have been employed for the immobilization of Co₄P₂. Photoanodes for solar water oxidation have been fabricated by depositing a thin film of diverse cationic polyelectrolytes and anionic Co₄P₂ on the surface of various photoelectrode materials using the layer-by-layer (LbL) assembly technique.¹⁸⁵ It was found that the performance of photoanodes was significantly improved after the deposition in terms of stability as well as photocatalytic properties, regardless of types of photoelectrodes and polyelectrolytes employed. Very recently, the Ag⁺ salt of Co₄P₂ was exploited as a hole extraction layer on the surface of BiVO₄ semiconductor photoanode for boosting photoelectrochemical activity by promoting hole extraction and transfer.¹⁸⁶ The BiVO₄/Co₄P₂ composite exhibited a pronounced water oxidation photocurrent density of 3.06 mA.cm⁻² at 1.23 V vs. RHE under (compared to the pure BiVO₄ 0.93 mA.cm⁻²), achieving a 3.3-fold improvement in photocurrent density. Furthermore, after the BiVO₄/Co₄P₂ photoanode was further treated by UV light irradiation, a photocurrent enhancement was achieved, bringing the photocurrent density to 4.03 mA.cm⁻², showing great potential for application in photo-electrocatalytic water oxidation.

For P- and Si- heteroatoms, Ru₄Si₂ displayed higher water oxidation activity than Ru₄P₂ under photochemical conditions. For that reason, Zhu et al. attempted to synthesize the Si-centered analog of Co₄P₂, but unexpectedly obtained the tetra-Co-sandwiched POM [Co₄(OH)(H₂O)₃](Si₂W₁₉O₇₀)]¹¹⁻

as a 1:1 mixture of two isomers (Co_4Si_2).¹⁸⁷ Although the Co_4Si_2 isomers are not analogous to Co_4P_2 , a comparative study under the conditions used in Co_4P_2 studies¹⁷⁰ showed that Co_4Si_2 is less efficient (lower maximum TON) and undergoes slow hydrolysis to more inactive forms during water oxidation. Following this work, Car et al. reported the analog compound to Co_4P_2 , $[\text{Co}_4(\text{H}_2\text{O})_2(\text{SiW}_9\text{O}_{34})_2]^{12-}$, and investigated its performance as visible-light-driven WOC at pH 5.8.¹⁶⁸ The Si-analog is an active WOC, although much less efficient than the original Co_4P_2 . In 2014, Lv et al. synthesized a new vanadate (V)-centered POM $[\text{Co}_4(\text{H}_2\text{O})_2(\text{VW}_9\text{O}_{34})_2]^{10-}$ (Co_4V_2), which is isostructural to Co_4P_2 .¹⁸⁸ Under photo-induced water oxidation, Co_4V_2 performs exceptionally fast (up to $\approx 10^3 \text{ s}^{-1}$ TOF) with final O_2 yields of $\sim 68\%$, twice as high as that of Co_4P_2 . The stability of Co_4V_2 has also been subject to debate.^{189,190,51,52} Recent vanadium NMR solution studies on the NMR/ Co^{II} aq/ CoO_x system describe a complex speciation behavior in solution, making the identification of the various equilibrating aqueous active catalysts in the system is a challenging task.¹⁹¹ Despite several advances, the large catalytic difference between Co_4V_2 and Co_4P_2 called for examining the significance of substituting phosphorus centers in Co_4P_2 with vanadium. A thorough DFT study on the OER mechanism for Co_4P_2 suggested that the O–O bond formation takes place from a Co^{3+} -oxyl radical through the WNA attack pathway.¹⁹² The computation of the reaction mechanism with Co_4V_2 showed a higher oxidation potential for the first proton coupled electron transfer (PCET) event and a reduction in the activation energy for the WNA pathway. The authors ascribed both effects to the decrease in the molecular orbital energies due to the orbital coupling between vanadium and cobalt atoms. In 2018, evidence for the significance of the vanadium centers to catalysis, predicted by theory, was found from soft X-ray absorption (XAS) and resonant inelastic X-ray scattering (RIXS).¹⁹³ The results revealed that Co_4V_2 possesses a smaller ligand field within the tetra-cobalt core and a cobalt-to-vanadium charge transfer band, supporting previous theoretical predictions. Interestingly, Soriano-López et al. recently reported that it is possible to dope molybdenum into the Co_4P_2 structure synthesizing a mixed Mo and W ($\text{Co}_4\text{Mo}_x\text{W}_y$) analog.¹⁹⁴ Doping the W framework of Co_4P_2 with Mo leads to the electrochemical oxidation of water at a low

onset potential, and with no catalyst degradation while reducing the overpotential of the oxygen evolution (η_{O_2}) reaction by 188 mV compared with the pure tungsten framework.

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Goberna-Ferrón et al. discovered the catalytic activity of the high-nuclearity Co-based POM $[Co_9(H_2O)_6(OH)_3(HPO_4)_2(PW_9O_{34})_3]^{16-}$ (Co_9).¹⁹⁵ Its molecular structure (Inset of Figure 15 (a)) contains three triads of edge-sharing $Co^{II}O_6$ octahedra supported by three tri-vacant Keggin-type $[PW_9O_{34}]^{9-}$ units. The triads are interconnected through three OH^- and two HPO_4^{2-} bridges. Six of the Co ions complete their coordination sphere with terminal water molecules. Co_9 is as an effective WOC using NaClO as the oxidant; when the ratio of catalyst to NaClO is 1:100, the reaction rate with Co_9 is at least 8 times faster than that with Co_4P_2 at pH 8. The catalytic process can be maintained for several days without fatigue or decomposition. The homogeneous character of Co_9 during the oxygen evolution reaction has been well established from postreaction characterization. In addition, small-angle X-ray scattering experiments were carried out to investigate, in detail, the speciation under catalytic working conditions, confirming the remarkable stability of Co_9 in water oxidation conditions.¹⁹⁶ As an electrocatalyst in homogeneous conditions, decomposition reactions that yield a thin CoO_x film on the anode can be easily avoided by the addition of chelating agents. After the reaction cycles, Co_9 can be recovered from solution by recrystallization with additional alkali-metal cations or by slow evaporation of the reaction medium. The Cs^+ insoluble salt of Co_9 can be blended into a carbon paste electrode to yield a robust catalytic process in the pH range from 1 – 8.¹⁹⁷ Co_9 -modified electrodes exhibited exceptional stability during bulk water electrolysis, where the current remains constant for at least 8 h. Moreover, $Cs-Co_9$ electrodes are more active than Co_3O_4 electrodes under the same conditions, yielding 2 orders of magnitude larger current densities for equimolar amounts of Co content (Figure 15 a). The most remarkable feature of $Cs-Co_9$ is its stability at a low pH values (<1.5), where CoO_x is unstable. This is important considering that acidic solutions appear to be preferred as media to carry out water electrolysis since hydrogen production is much easier at lower pH, where the proton (as reagent) concentration is higher. In this context, the Ba^+ salt of Co_9 showed a significantly better electrocatalytic performance in 1M H_2SO_4 than the Cs^+ salt, with onset

potentials as low as $\eta = 88$ mV (vs. 196 mV) and higher current densities due to better electron transfer kinetics.¹⁹⁸ Moreover, the Ba-Co₉ outperforms the state-of-the-art IrO₂ catalyst even at pH < 1, with an η_{O_2} of 189 mV at 1 mA.cm⁻². Notably, the authors observed an enhancement of the catalytic stability in acidic medium by using a carbon-paste conducting support with a hydrocarbon binder, which provides a hydrophobic environment. Very recently, the same authors reported a complete series of catalytic studies with multiple Co-based POMs, including Co₉, following the same working electrode strategy.¹⁹⁹ Composition-structure-activity relationships indicated that i) only those species containing P(V) as heteroatoms appeared to be stable; ii) the Keggin-derivatives exhibit faster performance than their Dawson-Wells counterparts; and iii) among them, catalytic activity is favored by high Co nuclearity and overall total charge. Since carbon paste is limited by its poor mechanical and redox stability, the authors recently turned their interest in conducting organic polymers, incorporating the Co₉ into a polypyrrole matrix to obtain organic-inorganic hybrid anodes.²⁰⁰ These electrodes sustain robust electrocatalytic water oxidation in neutral media, offering very good processability. It is remarkable that less than 6% POM content in a polypyrrole film multiplies OER currents by one order of magnitude, reducing the required overpotentials by approximately 200 mV. During these experiments, however, roughly 65% efficiency towards O₂ evolution was found, suggesting the occurrence of competing oxidations. It is also noteworthy that a Ba-Co₉/lead composite has been investigated recently as anode for OER during zinc electrowinning.²⁰¹

The OER is the most common anode or counter reaction in the electrowinning of metals from acidic electrolytes. Zn electrowinning consumes a lot of electrical energy due to the high η_{O_2} , so even a modest decrease in the η_{O_2} would be beneficial for industry to save energy. The η_{O_2} of the Ba-Co₉/lead composite decreased by about 137 and 40 mV compared to pure Pb foil and Pb-0.75Ag alloy (commonly used in the hydrometallurgical industry), respectively. Therefore, the Ba-Co₉/Pb composite could be a suitable substitute additive for Ag, with a strong potential industrial application. Recently, the Cs⁺ salt of Co₉ was tested as heterogeneous oxygen evolution catalyst in light-induced experiments, using Ru(bpy)₃²⁺ as the PS and S₂O₈²⁻ as the SA in neutral pH.²⁰² Post-catalytic assays

indicated that the Cs-Co₉ is transformed into the corresponding [Ru(bpy)₃]²⁺ salt upon cesium loss. Remarkably, analogous photoactivated oxygen evolution experiments starting with a [Ru(bpy)₃]²⁺ salt of Co₉ demonstrated much higher efficiency and kinetics, with maximum TON and TOF of 27.3 and 19.1 h⁻¹ respectively (14.2 and 10.8 h⁻¹ for Cs-Co₉), affording chemical yields close to 50% (10% for Cs-Co₉). The origin of this improved performance is the closer cation-anion (PS/catalyst) interaction in the solid state. This is beneficial for the electron transfer event, and for the long-term stability of the PS. Han et al. reported a series of high-nuclearity Co-based POM WOCs, ([Co₄(OH)₃(PO₄)₄)(XW₉O₃₄)₄)ⁿ⁻ (X = Si, Ge, P, As; n = 32, 28) (Co₁₆X₄).²⁰³ These Co-POMs contain a high-nuclearity Co–Pi cluster (Co₁₆(PO₄)₄(OH)₁₂) encapsulated by four [XW₉O₃₄]ⁿ⁻ units. The (Co₄(PO₄)₄(OH)₁₂) core contains a Co₄O₄ cubane structurally analogous to the [Mn₃CaO₄] core of the oxygen-evolving complex (OEC) in photosystem II (PSII). The trend in photocatalytic activity was Co₁₆Ge₄ > Co₁₆As₄ > Co₁₆Si₄ ≥ Co₁₆P₄. The values for Co₁₆Ge₄ were 31% O₂ yield, TON = 38.75 and initial TOF in the first 300 s of 0.105 s⁻¹. Furthermore, the structural integrity of the POMs under photocatalytic conditions was confirmed by recrystallization, laser flash photolysis, dynamic light scattering (DLS), phosphorous-31 NMR, UV–vis, POM extraction, and inductively coupled plasma mass spectrometry (ICP-MS). Recently, the photocatalytic activity towards water oxidation of Co₁₆P₄ has been compared to that of Co₉ and another Co-based POM, [Co₆(H₂O)₃₀(Co₉Cl₂(OH)₃(H₂O)₉(SiW₈O₃₁)₃)]⁵⁻ (Co₁₅).²⁰⁴ The WOC performance followed the trend Co₁₅ ~ Co₁₆ > Co₉, in agreement with flash photolysis results, indicating that fast multi-hole accumulation is a prelude to fast oxygen evolution under the conditions explored. The resident state of the Co-POMs after O₂ evolution displays XANES spectra that are consistent with a photo-induced oxidation of the cobalt centers while retaining the POM features, thus ruling out structural leaching of Co^{II} ions and evolution to CoO_x colloids.

Another high-nuclearity Co-based WOC that resembles the OEC in PSII is the double Co^{II}₄O₃ core POM [(A-α-SiW₉O₃₄)₂Co₈(OH)₆(H₂O)₂(CO₃)₃]¹⁶⁻.²⁰⁵ This octo-nuclear cobalt complex contains two cubical Co^{II}₄O₃ cores, with two of these Co atoms coordinated to terminal aquo ligands. The two

Co^{II}₄O₃ cores are located in two trivacant [SiW₉O₃₄]¹⁰⁻ ligands and are connected by three CO₃²⁻ anions. This catalyst exhibited excellent photochemical water oxidation activity, reaching a TON of 1436, currently the highest amongst bioinspired catalysts with a cubical core, and a high initial TOF of 10 s⁻¹. Zhang et al. combined the well-established bpy ligand and Co metal ion with stable Keggin-type Mo-POMs to design a robust organic-inorganic hybrid molecular WOC, [(Co^{II}bpy)₂(PMo₈^{VI}Mo₄^VO₄₀)₃[(Co^{II}bpy)(PMo₈^{VI}Mo₄^VO₄₀)]⁸⁻.²⁰⁶ This compound was shown to be an efficient visible light-driven catalyst for water oxidation. Its stability was demonstrated by DLS, POM extraction, UV-vis and FT-IR. Moreover, control experiments demonstrated that POM anions can enhance the WOC activity of bipyridine-substituted cobalt complexes. Chen et al. synthesized the first POM with a cobalt–arsenic core, [(Co^{II}₇As^{III}₆O₉(OH)₆)(A-α-SiW₉O₃₄)₂]¹²⁻, which contains two [SiW₉O₃₄]¹⁰⁻ fragments encapsulating a hepta-nuclear cobalt-arsenic (Co^{II}₇As^{III}₆O₉(OH)₆) core that show a “fused” double-quasi-cubane-type topology.²⁰⁷ The unique Co^{II}₇O₆ core provides another example of bio-mimetic structural model that catalyzes water oxidation. Very recently, Gong et al. reported a new sandwich tungstobismuthate WOC, (Hdamp)₂[(Na₄(H₂O)₉Co₂(H₂O)₆WO₃)₂(BiW₈O₃₀)₂] (dmap = N-(4-pyridyl)dimethylamine), which is an efficient catalyst for water oxidation under visible light irradiation at pH 9 (TON of 205.5 and O₂ yield of 32.88%).²⁰⁸ The basic structural unit can be described as two (BiW₈O₃₀)⁹⁻ POM units sandwiched by an unusual 14-nucleus mixed-metal cluster (Na₄(H₂O)₉Co₂(H₂O)₆WO₃)₂. Interestingly, the sandwich units themselves are directly interconnected to form independent chains and layers, forming extended 2D layers linked to each other by H-bonds and supramolecular interactions between the 4-dimethylaminopyridine (dmap) groups and surface oxygen atoms of the POM units. The stability of this catalyst was confirmed through UV-vis, DLS, catalyst aging, and POM toluene extraction experiments.

It is important to note that high cobalt nuclearity is not a requirement for POM-WOC design. In 2012, Tanaka et al. reported two POMs containing mono- and di-Co^{III} catalyst cores, [CoMo₆O₂₄H₆]³⁻ (Co-Mo) and [Co₂Mo₁₀O₃₈H₄]⁶⁻ (Co₂Mo), as the first examples of low nuclearity Co-

based POM WOCs.²⁰⁹ Photo-induced water oxidation at pH=8 revealed that both compounds possess higher activity than Co_4P_2 under the same experimental conditions, thus demonstrating that neither a critical POM size nor multi-site metal cores are mandatory for catalytic activity. The POM charges, normalized to the number of Co centers, are similar to each other (-3 , -3 , and -2.5 for Co-Mo, $\text{Co}_2\text{-Mo}$ and Co_4P_2 , respectively). Such an electronic factor may affect the O_2 evolving activity of cobalt centers. Moreover, the authors demonstrate that Mo-based POMs instead of W-based POMs can also serve as catalysts for O_2 evolution. Evangelisti et al. investigated sandwich-type $[(\text{Co}(\text{H}_2\text{O})_3)_2(\text{CoBi}_2\text{W}_{19}\text{O}_{66}(\text{OH})_4)]^{10-}$, with two identical lacunary ($\text{BiW}_9\text{O}_{33}$) units connected via two disordered ($\text{WO}_2|\text{CoO}_2$) internal groups and two terminal ($\text{Co}(\text{H}_2\text{O})_3$) moieties forming a tetranuclear metal core.²¹⁰ This POM exhibited high photocatalytic activity with maximum TON of 21 and 97% oxygen yield. However, the isostructural $[\text{Co}_{2.5}(\text{H}_2\text{O})_6(\text{Bi}_2\text{W}_{19.5}\text{O}_{66}(\text{OH})_4)]^{8-}$, that displays the same disorder pattern on the internal sites together with a 3:1 Co:W ratio on the terminal core positions, turned out to be inactive for water oxidation. The subtle difference in the Co occupancy of the terminal positions had a decisive effect on WOC activity, suggesting that only terminal core sites are essential for WOC activity and, therefore, that high nuclearity core clusters are not essential for the catalytic activity. A mono-nuclear Co^{II} -substituted POM, the Keggin $[\text{Co}^{\text{III}}\text{Co}^{\text{II}}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{7-}$, was investigated for visible-light driven water oxidation.²¹¹ The authors proposed that the $\text{Co}^{\text{III}}\text{O}_4$ tetrahedra, located in the center of the Keggin polyanion, plays an important role in maintaining the integrity of the structure, while the peripheral $\text{Co}^{\text{II}}\text{O}_6$ octahedral cluster is the active site for water oxidation. Notably, this Keggin POM catalyst was later applied to efficient hydrogen evolution under visible light irradiation.²¹² Another mono-nuclear Co^{II} -substituted POM, $[\text{Co}(\text{H}_2\text{O})_2(\gamma\text{-SiW}_{10}\text{O}_{35})_2]^{10-}$, was investigated as a light-driven WOC acquiring high TON of 313, a TOF of 3.2 s^{-1} , and Φ of 27% for O_2 evolution at pH 9.0.²¹³ Structural analogs incorporating Ni and Mn resulted in little water oxidation activity, suggesting that the Co center is the active site. In addition, the catalytic activity was better than that of the $\text{Co}^{\text{III}}\text{Co}^{\text{II}}$ Keggin POM discussed previously and comparable to that of Co_4P_2 under the same conditions. The hydrolytic stability of this mono-nuclear Co-POM was

confirmed by UV/Vis, linear sweep voltammetry measurements of the catalyst and by cathodic adsorption stripping analysis.

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4.1.3 Manganese-based POM WOCs

In natural photosynthesis, the WOC is a tetranuclear manganese cluster (Mn_3CaO_4) stabilized by amino acids, water molecules and counter ions. However, there are only a few examples of Mn-POMs reported. This lack Mn examples is not exclusive to POMs,²¹⁴ and even if one considers heterogeneous catalysts, Mn oxide is much less active than the corresponding Co or Ni analogs.²¹⁵ Still, the use of Mn is attractive because it is earth-abundant and relatively nontoxic when compared with the other more active metal-based catalysts.

Al-Oweini et al. reported the first manganese tungstate WOC, $[\text{Mn}^{\text{III}}_3\text{Mn}^{\text{IV}}\text{O}_3(\text{CH}_3\text{COO})_3(\text{SiW}_9\text{O}_{34})]^{6-}$, a mixed-valent (Mn_4) core, which is stabilized by a hybrid set of ligands, including an inorganic POM platform and carboxylate bridges.²¹⁶ The interplay of organic and inorganic residues provides a coordination environment with both stability and flexibility to assist stepwise one-electron oxidation of the catalytic core and to access high-valent Mn states that are responsible for water oxidation. Photo-induced water oxidation at pH 5 exhibited a TOF per Mn center of $0.71 \times 10^{-3} \text{ s}^{-1}$, TON up to 5.2, and a Φ of 1.7%. Schwarz et al. designed a Mn-based POM, $[\text{Mn}_4\text{V}_4\text{O}_{17}(\text{OAc})_3]^{3-}$, based on a $[\text{Mn}_4\text{O}_4]^{6+}$ cubane core stabilized by a $[\text{V}_4\text{O}_{13}]^{6-}$ ligand, that interacts with three Mn centers of the cubane, and three acetate ligands.²¹⁷ Under visible-light irradiation, the cluster shows high WOC activity (TON ~ 1150 , TOF $\sim 1.75 \text{ s}^{-1}$). Furthermore, the cluster stability and reactivity were checked by electrochemical, mass spectrometric and spectroscopic studies.

Recently, the photochemical and electrochemical water oxidation activity of the sandwiched dimer $[\text{Mn}_3(\text{H}_2\text{O})_3(\text{SbW}_9\text{O}_{33})_2]^{12-}$ was reported.²¹⁸ The authors demonstrated that heteroatoms in the POM play important role for the water oxidation; compared to its $[\text{PW}_9\text{O}_{34}]^{9-}$ and $[\text{AsW}_9\text{O}_{33}]^{9-}$ analogs, the Mn_3 -POM based on a Sb heteroatom has the best water oxidation activity. Multiple experiments including UV-vis, catalyst aging, POM extraction, electrochemical and capillary electrophoretic experiments confirmed that the catalyst is a homogeneous molecular catalyst. The

search for Mn-POMs which could exhibit WOC activity called for examining the Mn-analog of the well-studied $\text{Co}_4\text{P}_2, \text{Mn}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$.²¹⁹ Electrochemical water oxidation experiments showed initial activities comparable to those of the Co counterpart, although current density decreased very rapidly to become negligible just after 30 min, with the appearance of an inactive MnO_x layer on the electrode. Another high nuclearity Mn-POM, the mixed-valent $[\text{Mn}^{\text{III}}_{10}\text{Mn}^{\text{II}}_6\text{O}_6(\text{OH})_6(\text{PO}_4)_4(\text{A-a-SiW}_9\text{O}_{34})_4]^{28-}$ polyanion supported on graphene ($\text{Mn}_{16}@\text{graphene}$),²²⁰ was tested by using rotating ring-disk voltammetry (Figure 15 b) showing comparable TOF values to the Ru_4Si_2 -graphene system¹⁶⁴ at neutral pH. As shown in the inset of Figure 15 (b), the structure of this Mn-POM polyanion comprises a central $(\text{Mn}^{\text{II}}_4\text{O}_4)$ cubane, capped by 4($\text{Mn}_3(\text{SiW}_9)$) Keggin units. The overall assembly is connected to each other in a tetrahedral fashion by four phosphate (PO_4) linkers. This Mn-POM has been deposited on an ITO-coated glass electrode and on a glass carbon electrode by a layer-by-layer assembly method for electrocatalytic water oxidation.²²¹ Very recently, Teillout et al. synthesized and characterized the Mn-POM $[(\text{Mn}(\text{H}_2\text{O})_3)_2(\text{H}_2\text{W}_{12}\text{O}_{42})]^{6-}$, which is an extended 2-D network consisting of $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$ moieties linked together by Mn^{2+} , K^+ and Na^+ ions.²²² This complex undergoes multiple electron-transfer processes that lead to the electro-generation of manganese high-oxidation-state species that catalyze water oxidation.

4.1.4 Nickel-based POM WOCs

The first Ni-containing POM WOC, $[\text{Ni}_5(\text{OH})_6(\text{OH}_2)_3(\text{SiW}_9\text{O}_{33})_2]^{12-}(\text{Ni}_5\text{Si}_2)$ was reported by Zhu et al. in 2012.²²³ This Ni-POM was constructed from an *open Wells–Dawson* $[\text{Si}_2\text{W}_{18}\text{O}_{66}]^{16-}$ fragment (built up from two $[\text{SiW}_9\text{O}_{34}]^{10-}$ keggins-type subunits) embedded by a large $[\text{Ni}_5(\text{OH})_6(\text{OH}_2)_3]^{4+}$ unit in the central cavity. Ni_5Si_2 exhibited efficient chemical and photochemical water oxidation activity. Moreover, light-driven water oxidation revealed the formation of a Ni_5Si_2 –PS complex which exists in the form of NPs that remain molecular and do not decompose to nickel hydroxide particles, and which are more active for water oxidation than freely diffusing Ni_5Si_2 . Three polynuclear nickel clusters, $[\text{Ni}_{12}(\text{OH})_9(\text{CO}_3)_3(\text{PO}_4)(\text{SiW}_9\text{O}_{34})_3]^{24-}$,

$[\text{Ni}_{13}(\text{H}_2\text{O})_3(\text{OH})_9(\text{PO}_4)_4(\text{SiW}_9\text{O}_{34})_3]^{25-}$; and $[\text{Ni}_{25}(\text{H}_2\text{O})_2(\text{OH})_{18}(\text{CO}_3)_2(\text{PO}_4)_6(\text{SiW}_9\text{O}_{34})_6]^{50-}$ were reported as structurally stable WOCs under photochemical conditions (Figure 16).²²⁴ All three compounds contain (Ni_3O_3) quasi-cubane or (Ni_4O_4) cubane units, which are similar to the $[\text{Mn}_3\text{CaO}_4]$ core of the OEC in PSII. The trend in efficiency was $\text{Ni}_{12} < \text{Ni}_{13} < \text{Ni}_{25}$ (TON = 204.5), suggesting activity could be related to the Ni nuclearity.

Following this work, Yu et al. reported the photocatalytic activity towards water oxidation of a tetra-Ni-based POM, $[(\text{SiNi}_2\text{W}_{10}\text{O}_{36}(\text{OH})_2(\text{H}_2\text{O}))_4]^{24-}$.²²⁵ This Ni-POM can be seen as two lacunary $[\text{SiW}^{10}\text{O}^{37}]^{10-}$ Keggin units where each unit accommodates two Ni^{2+} ions linked together by two bridging -OH groups. The cluster shows higher WOC activity than the previously reported Ni-POMs, according to the O_2 yield (27.2%), high TON (335) and TOF of 1.7 s^{-1} . Singh et al. recently reported a hybrid POM-supported Ni^{II} coordination complex, $[(\text{Ni}^{\text{II}}(\text{bpy})_2(\text{H}_2\text{O}))(\text{HCo}^{\text{II}}\text{W}^{\text{VI}}_{12}\text{O}_{40})]^{2-}$, containing the Keggin anion $(\text{H}(\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40})^{5-})$ as the inorganic unit and 2,2'-bpy as the organic unit linked together with a Ni^{II} metal ion that acts as the catalytic center.²²⁶ This catalyst was found to be highly stable and robust under electrochemical water oxidation conditions at pH 7, exhibiting a moderate η value of 475.6 mV with a high TOF of 18.49 s^{-1} . However, the crystal structure of the compound was not investigated completely and hence more studies need to be conducted in order to tune the structure for real world applications.

4.1.5 Other POM WOCs

Several other POMs WOC have also been investigated. For instance, Cao et al. reported the first Ir-POM WOC, $[(\text{IrCl}_4)\text{KP}_2\text{W}_{20}\text{O}_{72}]^{14-}$.²²⁷ Its water oxidation activity was determined at pH 7.2 using $[\text{Ru}(\text{bpy})_3]^{3+}$ via electrochemical methods. Stability studies of the catalyst indicated a dissociation in aqueous solution into the $[\text{IrCl}_4(\text{H}_2\text{O})_2]^-$ unit and the $[\text{KP}_2\text{W}_{20}\text{O}_{72}]^{13-}$ ligand (based on 2 $\text{PW}_9\text{O}_{34}]^{9-}$ linked by two $[\text{W}^{\text{VI}}\text{O}_2]^{2+}$). However, the oxidation of water proceeds two orders of magnitude faster than the hydrolytic decomposition. Further water oxidation studies of the dissociation products indicated that both $[\text{IrCl}_4(\text{H}_2\text{O})_2]^-$ and IrCl_3 show similar activities, while the ligand $[\text{KP}_2\text{W}_{20}\text{O}_{72}]^{13-}$ is inactive to water oxidation, implying that the intact catalyst could well

catalyze water oxidation. However, this study was inconclusive regarding the formation of catalytically active IrO_2 NPs. Interestingly, a heteropolyoxoniobate compound, $[(\text{Nb}_2(\text{O})_2(\text{H}_2\text{O})_2)(\text{SiNb}_{12}\text{O}_{40})]^{10-}$, was reported as a water oxidation photocatalyst.²²⁸ The structure is composed of Nb-Keggin clusters linked into infinite 1D chains by dinuclear $(\text{Nb}_2(\text{O})_2(\text{H}_2\text{O})_2)$ moieties that contain a water molecule directly coordinated to each of the two bridging Nb active sites. Initial studies also demonstrated that this Nb-POM can be combined with a hydrogen-evolving catalyst (NiO), forming a heterogeneous system for the splitting of water into oxygen and hydrogen, albeit at relatively low TON.

Three new Ru dye-sensitized Mo-POM- $[\text{Ru}(\text{phen})_3]$ (phen = tris(1,10-phenanthroline)) hybrids were reported as active WOCs under photocatalytic conditions. $[\text{Ru}(\text{phen})_3\text{CH}_3\text{OH}][\text{Mo}_6\text{O}_{19}]$, $[\text{Ru}(\text{phen})_3][(\text{C}_2\text{H}_8\text{N}_2)_2(\text{C}_3\text{H}_7\text{NO})][\text{Mo}_5\text{S}_2\text{O}_{23}]$, and $[\text{Ru}(\text{phen})_3\text{CH}_3\text{CN}]_2[\text{Mo}_8\text{O}_{26}]$ were made of anionic Mo-POM clusters, charge-balancing $[\text{Ru}(\text{phen})_3]^{2+}$ PS unit and solvent molecules.²²⁹ The trend in catalytic efficiency was determined to increase with increasing Mo active sites. Impressively, the Ag^{I} -substituted Keggin POM $[\text{H}_3\text{Ag}^{\text{I}}\text{PW}_{11}\text{O}_{39}]^{3-}$ can be oxidized by $\text{S}_2\text{O}_8^{2-}$ in aqueous solutions to generate $[\text{H}_3\text{Ag}^{\text{II}}(\text{H}_2\text{O})\text{PW}_{11}\text{O}_{39}]^{2-}$ and a small amount of $[\text{H}_3\text{Ag}^{\text{III}}\text{OPW}_{11}\text{O}_{39}]^{3-}$, simultaneously evolving O_2 with higher efficiency than simple Ag salts.²³⁰ This work illustrated that the $[\text{PW}_{11}\text{O}_{39}]^{7-}$ ligand plays important roles in the transmission of both electrons and protons, and in the improvement of the redox performance of silver ions. In 2019, another Ag-based POM was reported by Chaojie Cui et al.,²³¹ $\text{H}_{17}[\text{Ag}_9(\text{AgH}_8\text{W}_{11}\text{O}_{44})_2(\text{bpy})_9]$, where $[\text{AgH}_8\text{W}_{11}\text{O}_{44}]^{13-}$ polyoxoanions are connected by 1D chains formed by Ag(I) cations ligated by bpy ligands to produce a 3D Ag(I)-containing POM-based MOF. This hybrid material exhibited photocatalytic O_2 production with an average rate of $964 \mu\text{mol.g}^{-1}$ in the first 10 minutes.

A POM WOC containing only vanadium atoms as metal centers, $[(\text{V}^{\text{IV}}_5\text{V}^{\text{V}}_1)\text{O}_7(\text{OCH}_3)_{12}]^-$, was reported in 2014.²³² The mixed-valence cluster is formally derived from the Lindqvist structure $[\text{M}_9\text{O}_{19}]^{n-}$ substituting the 12 μ -bridged oxo ligands by methoxo ligands. Under photoinduced

conditions, the Φ of 40% was comparable with the values obtained using one of the most studied Co(III) cubane-type species²³³ in similar conditions. The first Fe-POM WOC reported, $[\text{Fe}_{11}(\text{H}_2\text{O})_{14}(\text{OH})_2(\text{W}_3\text{O}_{10})_2(\text{SbW}_9\text{O}_{33})_6]^{27-}$ (Fe11)^{234,235} features six tri-lacunary Keggin $[\text{SbW}_9\text{O}_{33}]^{9-}$ ligands gathered together by a $(\text{Fe}_{11}(\text{H}_2\text{O})_{14}(\text{OH})_2(\text{W}_3\text{O}_{10})_2)^{27+}$ core. Under photochemical water oxidation, the TON reached 1815 with an initial TOF of 6.3 s^{-1} . Recently, Hu et al. implemented this catalyst into a three-component photocatalytic water oxidation system with BiVO_4 as light-harvesting material and NaIO_3 as SA. The system produced an O_2 yield of 19.1% sustaining initial TOF of 173 h^{-1} with a Φ of 25.3% in acidic medium.²³⁶ More recently, a well-known giant $\text{Mo}_{72}\text{Fe}_{30}$ POM cluster, $\text{Mo}_{72}\text{Fe}_{30}\text{O}_{252}(\text{CH}_3\text{COO})_{12}[\text{Mo}_2\text{O}_7(\text{H}_2\text{O})]_2[\text{H}_2\text{Mo}_2\text{O}_8(\text{H}_2\text{O})](\text{H}_2\text{O})_{91}$, has been explored as an efficient and stable WOC in the presence of light at pH 9 exhibiting TON of 13.99 with TOF of 3 min^{-1} .²³⁷ In a different strategy, Fe(III)-substituted anions, $[\text{PW}_{11}\text{O}_{39}\text{Fe}]^{4-}\text{O}^-$, were reported as oxo-donor ligands for hematite ($\alpha\text{-Fe}_2\text{O}_3$) cores (Figure 17 (a)), giving stable, water-soluble catalysts for water oxidation using visible light. The authors identified a new mechanism of freely diffusing fragments of solid-state metal oxide taking part in multi-electron oxidation of water.^{238,239} Yu et al. reported a Cu-POM WOC, the sandwich-type $[\text{Cu}_5(\text{OH})_4(\text{H}_2\text{O})_2(\text{SiW}_9\text{O}_{33})_2]^{10-}$, which was able to catalyze photochemical water oxidation with an O_2 yield of 12.3% and a TON of 61.²⁴⁰ Very recently, another sandwich-type Cu-POM cluster, $[\text{Cu}_3(\text{H}_2\text{O})_3(\text{SbW}_9\text{O}_{33})_2]^{12-}$ was shown to catalyze water oxidation at a neutral pH without decomposition under homogeneous electrochemical conditions.²⁴¹ Interestingly, $[\text{Cu}_5(\text{OH})_4(\text{H}_2\text{O})_2(\text{SiW}_9\text{O}_{33})_2]^{10-}$ showed negligible activity under the same conditions.

The molecular nature of POMs represent a unique opportunity for the development of WOCs. Furthermore, investigations have shown that the stability of the catalysts must be taken into consideration, studying the speciation and the mechanism of catalysis with POMs is essential for garnering fundamentally useful insights into catalysis by POM-based systems.

4.2 Oxygen Reduction

The reduction of molecular oxygen occurs inside fuel cells and metal-air batteries. The ORR follows very slow kinetics and has a very high overpotential. Therefore, significant research effort is devoted to improving this reaction. The reduction of molecular oxygen can occur through two pathways. First is the four-electron pathway, leading to the formation of water and second is the two-electron pathway in which the product is hydrogen peroxide (H_2O_2). POMs are normally used as active centers for a reduction supported over a conducting substrate to transport the electrons and accelerate the reaction kinetics.

4.2.1 POMs as Catalysts for ORR

In recent years, many POM compounds incorporating transition metal clusters have been shown to serve as robust catalysts, especially in the water oxidation field (section 4.1). However, relatively few reports have been devoted to the ORR catalytic activity of transition metal-substituted POMs. In 2015, Rousseau et al. reported a nanocomposite based on the heterometallic complex $[\text{Co}_7(\text{AlePyZn})_2]$ (Inset of Figure 17 (b)) and cost-effective VC XC-72 as ORR electrocatalyst.²⁴² This heterometallic POM complex contains a heptanuclear Co^{II} core sandwiched by two $[\text{PW}_9\text{O}_{34}]^{9-}$ units and connected to two $[\text{O}_3\text{PC}(\text{O})(\text{C}_3\text{H}_6\text{NHCH}_2(\text{C}_5\text{NH}_4))\text{PO}_3]^{5-}$ (AlePy) ligands linked to two Zn^{II} cations. Both Zn^{II} ions complete their coordination spheres with one oxygen atom of the POM and three terminal water molecules. The $\text{Co}_7(\text{AlePyZn})/\text{C}$ composite showed high activity for the reduction of O_2 (Figure 17 (b)), better tolerance to methanol crossover, which is important for practical applications of direct methanol fuel cells (DMFCs), and superior durability compared to commercial Pt/C. Recently, the same group reported a series of POM-based composites as efficient cathode materials for the ORR, in neutral or basic media, via a four-electron mechanism with high durability.²⁴³ Similarly to $\text{Co}_7(\text{AlePyZn})_2$, the reported POM structures consist of a M_7 ($\text{M} = \text{Co}$ or Ni) core encapsulated between two $[\text{PW}_9\text{O}_{34}]^{9-}$ units and structured by two alendronate (Ale, $(\text{H}_2\text{O}_3\text{PC}(\text{OH})(\text{C}_3\text{H}_6\text{NH}_2)\text{PO}_3)^{2-}$) ligands. The activity of this POM systems was optimized by the

judicious choice of 3d metals incorporated in the $((\text{PW}_9)_2\text{M}_7)$ ($\text{M} = \text{Co}, \text{Ni}$) POM core, the POM counter ions and the support (thermalized triazine-based frameworks (TTFs), fluorine-doped TTF (TTF-F), rGO, or carbon VC XC-72). In particular, the overpotential required to drive the ORR for the composite associating the $((\text{PW}_9)_2\text{Ni}_7)$ POM, $[\text{Cu}(\text{ethylenediamine})_2]^{2+}$ counter-cations, and the highly conductive and ORR active TTF-F carbonaceous material is very close to that of commercial Pt/C. The good ORR electrocatalytic activity can be attributed to two synergistic effects due to the binary combination of the Cu and Ni centers and the strong interaction between the POM molecules and the porous and highly conducting TTF-F framework. However, the mechanisms behind these synergies are still unclear and require further studies.

The well-known WOC $[\text{Co}_4(\text{H}_2\text{O})_2(\alpha\text{-PW}_9\text{O}_{34})_2]^{10-}$ (Co_4P_2) was tested as an ORR electrocatalyst in 2018.²⁴⁴ Co_4P_2 was immobilized onto different carbon nanomaterials (SWCNT, graphene flakes (GF), N-doped CNTs, and N-doped few layer graphene (N-FLG)). In alkaline media, all nanocomposites exhibited superior overall electrocatalytic activity when compared to the corresponding carbon materials with onset potentials (0.77–0.90 V vs RHE) comparable to commercial Pt/C (0.91 V vs RHE). In particular, $\text{Co}_4\text{P}_2@\text{N-CNT}$ presented greater diffusion-limiting current density (1.8 times) than Pt/C. Moreover, these nanocomposites showed excellent tolerance to methanol with no significant changes in current density, in contrast to Pt/C (decrease of $\approx 59\%$ after methanol addition), and good long-term electrochemical stability with current retentions between 75 and 84%. The integrity of the Co_4P_2 POM structure after the long-term stability tests was confirmed by XPS analysis.

Simple bare POM structures have also been reported as ORR electrocatalysts when combined with carbon-based materials. In 2014, a negatively charged Pressler-type POM, $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$, GO and poly(ethyleneimine) (PEI) were constructed into $(\text{PEI}/\text{POM-rGO})_n$ nanocomposite multilayer with protonated PEI via LbL self-assembly route combined with post-photoreduction method.²⁴⁵ The results obtained proved that the POM played a main role in ORR electrocatalysis while rGO promoted the advance of the onset potential, E_{onset} , for ORR to ~ 80 mV. Nunes et al.

prepared various nanocomposites based on vanadium-substituted phosphomolybdate, $[\text{PMo}_{11}\text{VO}_{40}]^{4-}$ (PMo₁₁V), incorporated into different carbon-based materials.²⁴⁶ All nanocomposites showed ORR electrocatalytic activity in acidic medium, with a strong dependency between the electrocatalytic ORR performance and the carbon material used as support. The E_{onset} shifted to less negative values in the order PMo₁₁V@carbon-black < PMo₁₁V@SWCNT < PMo₁₁V@graphene; for PMo₁₁V@graphene, the most promising composite, it was measured at $E_{\text{onset}} = 0.18$ V vs. RHE.

Recently, a lacunary Keggin POM, $[\text{PW}_{11}\text{O}_{39}]^{7-}$, was covalently linked with 3D ordered macroporous graphitic carbon nitride (3DOM g-C₃N₄) through an organic linker strategy.²⁴⁷ This covalent combination selectively promoted the two-electron O₂ reduction due to the enhanced O₂ adsorption of 3DOM g-C₃N₄-POM compared to its counterparts. The performance of the described POM ORR catalysts is summarized in Table 2.

4.2.2 POMs as Co-catalysts for ORR

POMs have also been combined with other materials to develop POM-based composites with improved catalytic properties for ORR as result of the synergetic effects between all components. Typically, Pt-based materials are state-of-the-art catalysts for ORR despite their high cost. However, due to the scarcity and high cost of noble metals, their integration with other sustainable and available materials such as POMs is an attractive way to optimize their properties and minimize their consumption. Additionally, using M⁰ nanostructures (i.e. zero-dimensional) increases the overall surface-to-volume ratio and hence reduces the metal loading. This is why great efforts have been focused on decreasing the Pt loading or replacing the electrocatalysts with non-Pt based materials.

Hsu-Yao et al. synthesized 3-4 nm sized POM-stabilized Pt⁰ NPs using electrochemically reduced POM anions, SiW₁₂O₄₀⁴⁻ and H₂W₁₂O₄₀⁶⁻, as reductant and protecting/stabilizing ligands.²⁴⁸ Compared to the commercial Pt black, both the POM-stabilized Pt⁰ NPs showed higher ORR, with Pt⁰@W₁₂O₄₀ NPs having better performance ($E_{1/2}$ showing a 30 mV positive shift while that of the Pt⁰@Si₁₂O₄₀ being 17 mV as compared to that of the Pt black). The observed activity enhancements may be related to the generally weakened reactant–metal surface binding as implied by cyclic

voltammetry (CV) analysis. In a different strategy, Renzi et al. recently evaluated the ORR catalytic activity of Pt⁰ NPs mixed with insoluble Cs₃HPMo₁₁VO₄₀^{249,250} and Cs₃H₂PMo₁₀V₂O₄₀²⁵¹ POMs. The Pt amount was reduced through the use of POMs as co-catalytic supports that are able to: i) enhance catalyst dispersion and limit the aggregation during fuel cell operation, induced by the mesoporous features of POM that allow the embedding of Pt inside the micro-mesopores; and ii) enhance the kinetics of the ORR redox process, owing to the high surface acidity of POMs and consequent high proton mobility. This strategy allowed decreased Pt loading while maintaining the electrocatalytic performance towards ORR.

Xin et al. fabricated stable Au⁰ NPs/POM modified glassy carbon electrodes (GCE) using LbL assembly. PPDA-stabilized Au⁰ NPs were synthesized first using NaBH₄ as reducing agent.²⁵² Next, GC/(POM/Au-NP)_n LbL hybrid films were prepared by the sequential deposition PDDA-stabilized Au⁰ NPs and POMs on GCE via the electrostatic forces between the negatively charged POM and positively charged PDDA. The authors compared the electrocatalytic behavior in terms of half-wave potential for the ORR ($E_{1/2}$) of LbL monolayers built using W-, Ru-, and Co-substituted Keggin POMs. The trend in catalytic activity was PCoW₁₁O₃₉⁵⁻ > PRuW₁₁O₃₉⁵⁻ > PW₁₂O₄₀³⁻, where POM co-catalysts containing more labile M–O bonds (e.g. Co-substituted) were better ORR co-catalysts. In the same year, Bao et al. chose a wheel-shaped V^V–V^{IV} mixed-valence tungstovanadate, [P₈W₄₈O₁₈₄(V₄^V V₂^{IV}O₁₂(H₂O)₂)₂]³²⁻ (V₁₂), that acts as both reducing (V^{IV} reduced centers in V₁₂) and capping ligand to synthesize 30 nm POM-stabilized Au⁰ spherical NPs (Au⁰@V₁₂ NPs) in a one-pot procedure.²⁵³ The negatively-charged surface of the Au⁰@V₁₂ NPs allowed the easy fabrication of multilayer films on ITO-coated electrodes based on the electrostatic attraction with the positively charged PEI using a LbL assembly method (Figure 17 (c)). CV experiments indicated the Au⁰@V₁₂ NPs based composite films possessed good electrocatalytic activities in ORR.

Reduced POMs (rPOM) are extremely stable in alkaline solutions and can participate in electrocatalytic cycles. In 2015, a rPOM was used as assistant catalyst substrate for Pd⁰ NPs.²⁵⁴ In the synthetic procedure, (NH₄)PMo^{VI}₁₂O₄₀ POM was reduced (*in situ*) using NaBH₄ at the same time as

the Pd^{2+} salt was reduced to form a $\text{rPOM}@ \text{Pd}^0$ hybrid with the Pd^0 NPs sitting on the surface of the rPOM . The use of rPOM as a support for Pd^0 NPs not only enhances the stability of the Pd^0 NPs via powerful support interactions minimizing the agglomeration but also efficiently enhances the ORR activity of the Pd^0 NPs via electron transfer between Pd^0 and rPOM . This $\text{rPOM}@ \text{Pd}^0$ hybrid showed better electrocatalytic performance for ORR in alkaline media than the commercial Pt/C EC: $E_{\text{onset}} = 1.078 \text{ V vs. RHE}$ (0.051 V more positive compared to Pt/C EC) and almost no declining of catalytic activity during 1500 cycles. The performance enhancement is a result of the changes in the electronic structure of Pd^0 induced by synergistic interaction with the rPOM support, which weakens the interaction between Pd^0 and non-reactive oxygenated species (e.g. H_2O_2), providing more active sites for O_2 adsorption and activation.

Taking advantage of the high surface area and electrical conductivity of nanocarbons and their ability to be hybridized with POMs, several POM and carbon-based composites have been tested as ORR electrocatalysts. For instance, Wang et al. introduced a novel $\text{Pd}^0/\text{POM-PDDA-MWCNTs}$ composite with high electrocatalytic activity for the ORR of fuel cells (Inset of Figure 18 (a)).²⁵⁵ The construction implied the immobilization of Keggin-type tungstophosphoric acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$, PW_{12}) on the outer walls of MWCNTs functionalized by PDDA via the electrostatic forces between the negatively-charged PW_{12} and positively charged PDDA, followed by reductive deposition of Pd. The highly dispersed $\text{Pd}^0/\text{PW}_{12}$ NPs supported on PDDA-MWCNTs showed a much higher ORR activity (in terms of kinetic current density (I_k), defined as the current in the absence of mass-transfer limitations) than acid-treated MWCNT-supported Pd catalysts and comparable activity with that of commercial Pt/C catalysts as seen in Figure 18 (a). The authors suggest that PW_{12} could act as both the effective mediator and as a source of mobile protons at the electrocatalytic interface. Moreover, XPS data indicate that the composite material possesses a significantly higher amount of metallic Pd compared with Pd/acid treated-MWNTs, and it would facilitate desorption of adsorbed oxygen. This is a critical parameter to maximize electrode performance, as limited oxygen desorption and bubble formation on the electrode can significantly increase the overpotential.

More recently, a novel Pd⁰/POM/rGO nanocomposite was prepared by the assistance of H₃PMo₁₂O₄₀ (PMo₁₂) and hydrazine hydrate as reducing agent.²⁵⁶ The electrostatic repulsive interactions derived by PMo₁₂ anions effectively prevented the agglomeration of Pd⁰ NPs, which were uniformly distributed over the surfaces of rGO. The composite revealed enhanced catalytic activity compared to its counterparts, as indicated by the higher current density on the linear sweep voltammograms (LSVs). Moreover, when methanol is added the LSV remains the same, demonstrating that the Pd⁰/PMo₁₂/rGO catalyst has an excellent tolerance to the methanol cross-over effect.

Initial steps have been taken to replace the traditional noble-metal particles for the ORR by cheaper metals. POM-stabilized Ag⁰ NPs on CNTs²⁵⁷ or rGO²⁵⁸ were prepared by a facile one-pot synthetic procedure using *in situ* photo-reduced PW₁₂ Keggin anions as reducing agent and capping ligands. These nanohybrid tri-component systems were shown to be competitive to the commercial Pt/C for ORR. Using an alternative synthetic method, 2D Ag⁰ nanonets (NN)@POM–graphene nanosheets (GNSs) were reported.²⁵⁹ The composite was prepared using a Mo^V/Mo^{VI} mixed-valence POM, H₇[β-PMo₄^VMo₈^{VI}O₄₀], as the reducing, encapsulating and bridging agent to deposit an Ag⁰ nanostructure on graphene. The as-prepared ternary Ag⁰NN@POM–GNS composites showed high electrocatalytic ORR activity, with more positive onset (*E*_{onset}) and cathodic peak (*E*_{pc}) potentials and higher cathodic peak current density (*i*_{pc}) compared to the binary Ag⁰NN@POM composites. The authors attribute the excellent performance to the high catalytic activity of the Ag⁰NN and the excellent electron transfer properties of GNSs, and their synergistic effect reinforced by the POM presence.

Liu and co-workers reported the electrochemical-reduction-assisted assembly of ternary Ag⁰NPs@PW₁₂–rGO,²⁶⁰ where the POM worked as both electrocatalyst and capping ligand as displayed in Figure 18 (c). This composite showed much better electrocatalytic activities towards the ORR than binary Ag⁰NPs@PW₁₂ and PW₁₂/rGO nanohybrids, with higher *i*_{pc} and a more positive *E*_{onset} and *E*_{pc} values. Moreover, these results proved that the hybrids were sufficiently competitive

with commercial Pt/C. More recently, a PW_{12} -modified $Ag@Pt/MWCNT$ electrocatalyst was prepared by electrostatic interaction with positively charged chitosan-functionalized core-shell $Ag@Pt$ NPs on MWCNTs.²⁶¹ The results showed that PW_{12} improves the electrocatalytic activity of $Ag@Pt$ NPs; with a $E_{1/2}$ (half-wave electrode potential) for the ORR which positively shifted 44 mV from that of $Ag@Pt$ NPs/MWCNTs, and a mass activity (I_m) and specific area activity (I_s) about 2 times higher than those of $Ag@Pt$ NPs/MWCNTs. The enhanced activity can be explained by the protective effect of the PW_{12} layer on the catalyst surface. The negative surface potential established over the catalyst surface protects complex metal anions from being subjected to electrostatic repulsion thereby conserving the active metal species on the catalyst surface. The performance of Nano-Heterostructure POM is summarized in Table 3.

In the search for Pt-free catalysts, considerable efforts have also been devoted to investigating metalloporphyrin catalysts for ORR, particularly Fe or Co porphyrin complexes.²⁶² However, little attention has been given to the combination of cationic metalloporphyrins and anionic POMs. In 2012, a PW_{12} /porphyrin composite based on a mixture of cationic [5,10,15,20-tetrakis(1-methyl-4-pyridinio)porphyrin]cobalt(II) (CoPP) and anionic PW_{12} supported on carbon black was reported as an active ORR electrocatalyst.²⁶³ The results showed that cobalt ion was vital for the formation of the active ORR species, but might be attributed to the interaction of Co with POM that significantly improved the ORR activity. Hybrid ORR electrocatalysts have been prepared by ionic self-assembly of positively charged Fe(III) *meso*-tetra(*N*-methyl-4-pyridyl) porphyrin (FeP) with negatively-charged PMo_{12} in the presence of suspended MWCNTs.²⁶⁴ Figure 18 (b) shows the schematic illustration of steps involved in the synthesis of hybrid ORR catalyst. Compared with individual PMo_{12} and FeP, the hybrid FeP/ PMo_{12} -MWCNT electrocatalyst demonstrated a much higher ORR activity in terms of E_{onset} and $E_{1/2}$ in acidic media due to the high proton conductivity of PMo_{12} together with the large surface area and high electrical conductivity from the MWCNTs.

Interestingly, Deng's group has developed a liquid-catalyst-mediated fuel cell (LCFC) employing only Mo–V–P POM solutions as electrocatalysts and constructed using a Nafion 115

membrane sandwiched between two 3D graphite electrodes with no metal loading.²⁶⁵⁻²⁶⁷ In these cells, a Keggin-type $\text{H}_3\text{PW}_{11}\text{MoO}_{40}$ solution oxidizes the biomass under sunlight or heating (at the anode), while a modified (non-Keggin) $\text{H}_{12}\text{P}_3\text{Mo}_{18}\text{V}_7\text{O}_{85}$ aqueous solution leads to the reduction of oxygen (in the cathode). The two POM solutions have different redox potentials and, unlike noble-metal catalysts, have the advantage of being tolerant to catalyst-poisoning organic and inorganic contaminants. Therefore, raw biomasses, such as cellulose, starch, and even grass or wood powders can be used directly to produce electricity without prior purification. It is noteworthy that, contrary to conventional fuel cells, in which small molecules such as hydrogen and methanol are the best fuels, biomass fuels are more favorable for this novel LCFC with respect to their power densities. In another study, Mo–V–P POM solutions, $\text{H}_{3+x}\text{PV}_x\text{Mo}_{12-x}\text{O}_{40}$ ($x = 0, 2, \text{ and } 3$), were applied as redox mediators for the ORR in polymer electrolyte fuel cells.²⁶⁸ In this electrochemical system, the POM is reduced over the carbon cathode, and then the resultant rPOM is re-oxidized by exposure to the dissolved oxygen in the regenerator. The substitution quantity of V in the POM significantly affected the onset reduction potential as well as the current density achieved; $\text{H}_6\text{PV}_3\text{Mo}_9\text{O}_{40}$ was the most suitable mediator in terms of the electrochemical reduction property. The principle of using POM solutions and carbon as the cathode ORR catalyst can provide new methods for the improvement of other fuel cell systems.

4.3 Other Catalytic applications

4.3.1 Carbon dioxide reduction reaction

The increasing concentration of atmospheric CO_2 due to the industrial era is alarming and has now crossed the threshold of 400 ppm.²⁶⁹ Although massive emission of CO_2 has resulted in serious environmental problems, it still is an important non-toxic, highly abundant and cheap carbon feedstock. Photo/electrocatalytic carbon dioxide reduction reaction (CO_2RR) represents a favorable means that can reduce CO_2 to highly valued hydrocarbon fuels or chemicals by using renewable solar energy or electricity as driving force. For CO_2RR , the most important and ambitious goal is to realize

the efficient, selective and durable transformation of CO₂ into specific product with a view to increasing the possibility of large-scale utilization. The major challenge is to develop efficient catalysts for CO₂RR. The desirable photocatalyst for CO₂RR should at least have following features: i) a suitable band gap structure for absorbing photons; ii) an efficient separation and transport of photo-generated electron-hole pairs; iii) large number of active adsorption and reaction sites for promoting photocatalytic reaction.²⁷⁸⁻²⁸⁰

The research in photocatalytic CO₂RR is focused on finding catalysts that can work in visible light (>380nm) and are able to sustain the multi-electron transfer process. The final products of such a process are carbon monoxide (CO), formic acid (HCOOH), formaldehyde (HCHO), methanol (CH₃OH), and methane (CH₄).^{270,271} It is noteworthy that some of the end products of this reaction are useful in their own right. For example, formic acid is a very promising hydrogen carrier and an important reagent in organic synthesis processes. POMs as one kind of molecular photocatalysts that display quasi-semiconductor photochemical properties also have many advantages in performing CO₂RR, such as superior solution, thermal stability and adjustable redox potential and reversible redox activity, which have also been reflected in photocatalytic HER and OER. Their good solution stability can enable them to carry out photocatalytic CO₂RR in water or other solvents, and their own redox properties can assist the multi-electron and multi-proton transfer process required for the conversion of CO₂ to products. Of course, the research on CO₂RR based on POM-based photocatalysts is still in its infancy, some meaningful conclusions need to be obtained based on more investigations. Neumann and co-workers²⁸³ demonstrated the first practical utilization of Ru^{III} substituted Keggin structure, [(C₆H₁₃)₄N₅][Ru^{III}-(H₂O)SiW₁₁O₃₉] for the photoreduction of CO₂ to CO with Et₃N as reducing agent. DFT calculations suggests that CO₂ is preferably coordinated in a side on manner to Ru^{III} in the POM through formation of a RuO bond, further stabilized by the interaction of the electrophilic C atom of CO₂ to an O atom of the POM. The interaction of the nucleophilic O atom of CO₂ to Ru atom and the formation of O₂C-NMe₃ zwitterion stabilize both Ru-O and C-N interactions and determine the promotional effect of an amine on the activation of CO₂ by

POM molecule. Besides, several approaches are employed to construct heterogeneous crystalline POM-based photocatalysts for CO₂RR. Recently, Lan et al.²⁸⁸ prepared several efficient heterogeneous POM-based photocatalyst systems and demonstrated an effective reduction of CO₂ to CH₄ with high selectivity and activity. They first synthesized two pure inorganic POM-based frameworks constructed with strong reductive [P₄Mo₆V] units, NENU-605 and NENU-606, both of which can be used as heterogeneous catalysts for photocatalytic CO₂RR. It should be noted that this is the first POM-based crystalline photocatalysts system to reduce CO₂ to CH₄ in water with a high selectivity of 85.5%. In this work, the strong reductive [P₄Mo₆V] units serving as multielectron donor played a crucial role in promoting the 8 electrons and 8 protons transfer process required for CO₂-to-CH₄ conversion. These works indicate that developing strong reducing POM into photocatalyst architecture can increase the possibility of reducing CO₂ to CH₄ or other high-value carbon-based products accompanied with multiple processes. Table 4 shows the examples of best POM based photocatalysts for CO₂RR.

Reducing CO₂ into value-added fuels (such as C₂H₄, CH₄, CO) or chemicals (such as HCOOH, CH₃OH, C₂H₅OH) is one of the promising paths to address environmental issues and affords a convenient solution for energy conversion. Compared with the photocatalytic CO₂ reduction, electrical energy-driven CO₂ reduction is also an effective technology to realize this reaction process and commonly shows higher conversion efficiency. The brief list with their standard reduction potential and chemical reaction can be found in a paper by Qiao et al.²⁷² Nevertheless, HER as competitive reactions in aqueous electrolytes reduces the conversion efficiency of CO₂ during the electrochemical process due to their comparable thermodynamic potential. Therefore, the search of superior electrocatalysts with excellent electrochemical activity and suppressive HER is of great importance to develop CO₂RR. An ideal electrocatalysts for CO₂RR are expected to have following characteristics: i) flexible redox ability for the multielectron transfer, ii) high Faradaic efficiency and selectivity for the CO₂RR, iii) high structural and performance stability during a long-term electrochemical process, iv) high catalytic activity with a low electrochemical overpotential, and v)

scalable synthesis from low cost raw materials. Recent focus is on the development of heterogeneous electrocatalysts in nanostructured form, while the contrary homogeneous electrocatalysts mainly involve molecular metal complexes and macrocyclic organics.

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Owing to the capability of POMs to undergo reversible multi-electron redox reactions without decomposition, they can be used along with a co-catalyst that brings down the activation energy for CO₂ reduction. Moreover, POMs as weak bases could promote the formation of hydrogen-bond networks near the CO₂ coordination center to favor proton-coupled electron transfer that occurs when the proton source is close to the catalytically active center. Electrocatalytic reduction of CO₂ with POM was first reported by Kozik et al.²⁷⁸. It was observed that α -[SiW₁₁O₃₉Co]⁶⁻ showed the electrocatalytic activities for CO₂ reduction, however, the final CO₂ reduction product was unstated. More than decade later, Proust et al. reinvestigated this reaction in more detail by using $[\alpha$ -SiW₁₁O₃₉Co]⁶⁻ in the electro-assisted reduction of CO₂.²⁹⁰ The $[\alpha$ -SiW₁₁O₃₉Co]⁶⁻ contained a Co^{II} in place of a W^{VI}. The square-pyramidal CoO₅ with a vacant site was generated by losing a coordinated water molecule from CoO₅(H₂O) octahedral when the POM was extracted from aqueous to organic media. Except CO and HCHO, neither H₂ nor other CO₂ reduction products were detected. This indicated the unique selectivity of $[\alpha$ -SiW₁₁O₃₉Co]⁶⁻ POM catalyst in the electroreduction of CO₂. The turnover of CO₂ to CO reached to 3.7 with the faradic efficiency of 13%. HCHO was the other detectable product with amount varied from 2.1×10^{-7} to 2.2×10^{-6} mol with the faradic yield varying from 25% (high HCHO content with low electrolysis charge) to 0.8% (low HCHO content with high electrolysis charge). Likewise, Wang et al has investigated MOFs as co-catalysts and combined them with POMs.²⁷³ The bonds between Zn²⁺ ions on POM and carboxylates porphyrin were formed under hydrothermal conditions using M-TCPP = tetrakis[4-carboxyphenyl]-porphyrinato-M, as ligands. Here M is for metal Co, Fe, Ni and Zn. The electrochemical performance of the reduction reaction was evaluated in an airtight three-electrode electrochemical H-type cell, where a proton exchange membrane (Nafion® 212) separated the compartments. The performance of different metal POM-MOF are summarized in the Table 5. The mechanism of CO₂ reduction in presence of POM and effect

of temperature on reduction reaction initiated by different driving forces needs to be investigated further to develop this technology for commercial application.

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4.3.2 Nitrogen reduction reaction

Nitrogen (N_2) makes up 78% of the total gaseous composition of the atmosphere. However, fixing nitrogen in soil is still difficult but important reaction needed to maintain the global ecosystem. To supply the necessary nitrogen to plants, ammonia is produced using the Haber–Bosch approach, which is energy intensive and carried out under harsh conditions. Hence, finding alternative ways or catalysts for the nitrogen reduction reaction (NRR) is crucial. Recently, Li et al used a typical MOF material, zeolitic imidazolate framework-67 (ZIF-67) with network tetrahedral topologies to adsorb N_2 on its porous structure.²⁷⁴ The ZIF-67 was combined with various transition-metal-substituted POMs to supply multiple electrons to efficiently carry out NRR. Their performance towards NRR was evaluated in a sealed reactor with 300 mg of photocatalyst, 80 mL of distilled water and 20 mL of ethyl alcohol. The reaction was carried out at room temperature and N_2 was introduced in the reaction vessel at 1 L/minute, for an hour. As seen from Figure 19 (a), the ZIF-67/POM composite nanomaterials showed higher catalytic performance than that of ZIF and POMs alone with highest N_2 fixation efficiency reaching 149.0 $\mu\text{mol/L}$ at 1 h, yielding a solar to ammonia (STA) efficiency of 0.032 % for ZIF-67@ PMo_4V_8 . The energy levels and electron-transfer mechanism for ZIF-67 and POMs composite photocatalyst is shown in Figure 19b. Accordingly, the porous ZIF-67 adsorbs a large amount of N_2 while the POMs are reduced under light conditions, and the reduced POMs more easily stimulate electrons to participate in the catalytic process. After the reaction, the reduced POMs react with the oxidant (e.g., O_2) to turn into their oxidized state and forms a complete self-healing and circulatory system (Figure 19b). Another important example of POM-based catalyst for NRR is demonstrated by Wang et al.²⁷⁵ They used $\text{PMo}_{12}\text{@MOF-100(Fe)}$ POM with PVP (polyvinylpyrrolidone) as a precursor to synthesize two FeMo-based electrocatalysts, $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7/\text{FeS}_2\text{@C}$ and $\text{FeMoO}_4/\text{FeS}_2\text{@C}$ by hydrothermal methods. The

$\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7/\text{FeS}_2@\text{C}$ showed outstanding catalytic performance with a high NH_3 yield rate (105.3 $\mu\text{g h}^{-1} \text{mgcat}^{-1}$) and Faradaic efficiency (54.7%) in acidic electrolytes at -0.4 V vs. RHE, which is higher than $\text{FeMoO}_4/\text{FeS}_2@\text{C}$, and most reported electrocatalysts for NRR. Further electrochemical experiments in alkaline electrolytes reveal the overall NRR catalytic activity of $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7/\text{FeS}_2@\text{C}$ (NH_3 yield of 86.3 $\mu\text{g h}^{-1} \text{mgcat}^{-1}$, FE of 53.6% at -0.4 V vs. RHE). The NRR performances of POM based catalysts is summarized in Table 6.

4.3.3 Biomass conversion using POMs

Due to the oxygen rich characteristics of biomass, POMs are now being investigated to catalyze biomass conversion reactions for obtaining valuable oxygen-containing chemicals. Along these lines, Voß et al investigated the conversion pathway of glucose using either an oxygen or a nitrogen atmosphere.²⁷⁶ The reaction was catalyzed by Lindqvist-type POM $\text{K}_5[\text{V}_3\text{W}_3\text{O}_{19}]$. The time dependent distribution of products of the above catalyzed reaction is shown in Figure 20. Further, the Keggin type POM catalyst $\text{H}_6[\text{PV}_3\text{Mo}_9\text{O}_{40}]$ and a substrate variation (glucose and glyceraldehyde) was also tested under aerobic (oxygen) and anaerobic (nitrogen) environment (see Table 7). It was found that the substrate and the reaction conditions (whether it is aerobic or anaerobic) determine the final product (folic acid (FA), or lactic acid (LA)). Hence, it is shown that a suitable catalyst can be chosen, which can be combined with a given set of parameters to convert biomass into the desired chemical/s.

Liu et al used various kinds of biomass (cellulose, lignin and even wood and grass powders) in a novel electrolytic reduction process at low temperature.²⁷⁷ The process was catalyzed by a POM solution as depicted in figure below. No current was observed initially at an applied potential of 1.1V, even in the presence of glucose. However, when a PMO_{12} solution was pumped through the anode along with biomass, a sharp increase in the electrolysis current was observed together with the corresponding bubbles of H_2 gas at the cathode side as can be seen from Figure 21 (a, b). The use of POMs to produce H_2 at low electric energy consumption from biomass is very young but promising

technology that remains to be deeply explored. Various parameters such as temperature, active sites on the POM, electrolyte effect and electron transport paths need further investigation.

Anna Bukowski et al developed a concept called the Ionosolv method in which fractionation of lignocellulosic biomass (wood) was achieved using a low-cost IL.²⁷⁸ Bio-derived formic acid was produced using a POM catalyst and molecular oxygen as an oxidant. The IL alkylammonium [TEA][HSO₄] was used as a solvent to break down the lignocellulosic feedstock. The best performance was achieved using vanadium substituted POM (H₈[PV₅Mo₇O₄₀]) with respect to folic acid yield (23%) from hardwood (beech), which corresponds to a folic acid selectivity of 54%. The Ionosolv method was also used with other types of wood such as softwood (pine) and grass biomass (Miscanthus). This method should be evaluated further for final product purity, catalyst recyclability and cost effectiveness of the whole process. This step will test the commercial viability of the concept.

4.3.4 Methanol oxidation using POMs

Direct alcohol fuel cells (DAFCs) are systems that extract energy by selective oxidation of the alcohol. Hydrogen ions produced by alcohol oxidation are transported across the proton-exchange membrane to the cathode, where they react with O₂ to form water. The overall reaction occurring in a DAFC is $2 C_n H_{2n+1} OH + 3 n O_2 \rightarrow 2 n CO_2 + 2 (n+1) H_2 O$. DAFCs have been also proposed as the green energy for future vehicles due to its easy fuel storage, high energy density and low emission of pollutants.²⁷⁹ The most widely studied ones utilize methanol and ethanol and are referred as a direct methanol fuel cell (DMFC) or a direct ethanol fuel cell (DEFC), respectively. Several efforts have been devoted in the past years to develop efficient catalysts and are outlined in the previous review articles. For instance, platinum²⁸⁰ based or nano-metals (noble and non-noble)²⁸¹ catalysts with their potential application in portable devices²⁸² due to high energy density and easy handling among others. In this section, we have highlighted key features and complement the abovementioned reviews with the most important investigations that have reported POMs-based catalytic reactions.

Pt is commonly employed as the catalyst in acidic media in DMFC or DEFC devices. However, Pt on its own is not a highly efficient catalyst due to poisoning from the strongly adsorbed

species such as $\text{CH}_{(\text{ad})}$, $\text{CH}_{3(\text{ad})}$, and $\text{CO}_{(\text{ad})}$ generated during oxidation. Accordingly, many efforts have been dedicated to improve the poisoning tolerance of the metal. Normally researchers encounter partial oxidation to aldehydes, ethers or carboxylic acids²⁸³⁻²⁸⁵ therefore the system is not extracting all the power of the system. Most of the papers reviewed here are uses commercial POMs (as seen in Table 8), but as an anti CO poisoning agent of the real catalyst (which is Pd, Pt, Ru, Au or composites) and/or morphology control rather than alcohol oxidation. For example, Shi et al²⁷⁹ studied the performance of Pt/Pyridine ionic liquid POM/rGO ($\text{Pt}/(\text{epy})_3\text{PMo}_{12}\text{O}_{40}/\text{rGO}$) in acidic conditions, suggesting improvement in the reaction. The reason attributed to the fact that POM promote uniformity of Pt dispersion ((111) face) and exhibits anti-CO poisoning properties. This is one of the main conclusions extracted from the past research in the field as the POM improve the crystal size homogeneity and decrease the size. The second conclusion is that POMs improve the catalyst stability by preventing the surface poisoning with by-products that are strongly adsorbed.²⁸⁶⁻²⁸⁸ However, Barczuk et al.²⁸⁹ doubts the electron mediating function of the PMo_{12} in the electrooxidation of ethanol, despite the fact the chronoamperometric results evident an increase in current and stability of the metal catalyst (Pt, Pt-Ru, Pt-Sn/C etc.). They propose that PMo_{12} stabilize the oxo-groups on top of metal, which are known to induce the oxidation of the poisoning species (such as CO).

Various POMs have been proposed and tested as additives for methanol oxidation including PMo_{12} , SiW_{12} , PW_{12} ,^{290,291} wheel-shaped VV –VIV mixed-valence tungstovanadate (V_{12}),²⁵³ and their composites. Of special interest, Bommineni S et al.²⁸³ investigated the methanol oxidation with pure PMo_{12} and three derivative (pyridine, niobium and pyridine-niobium salt). The authors analyse the methanol oxidation under a gas stream (Ar , O_2 MeOH) at 533K adjusting the conversion around 10%. It was revealed that the PMo_{12} and its niobium salt give mainly dimethoxymethane while the niobium pyridine derivative gives preferentially dimethyl ether. The pyridine POM salt gives mixture of the products. Likewise, Chen et al.²⁹² studied the influence of WO_x and PW_{12} on the PtRu/C catalyst, suggesting an improvement in the catalytic properties due to both: 1) WO_x facilitates the nanoparticles distribution on carbon while 2) PW_{12} improve the poison resistance behaviour of the

catalyst. Similarly, the catalytic effect of a complex POM ($\text{H}_{3+x}\text{PMo}_{12}\text{V}_x\text{O}_{40}$ ($x = 0, 1, 2, 3$)) and surface-supported $\text{VO}_x/\text{H}_3\text{PMo}_{12}\text{O}_{40}$ was also investigated.²⁹³ The study was performed in isothermal fixed bed reactor with a gas stream at 250°C. The volume composition of the gaseous reactant feed was 6% CH_3OH , 13% O_2 and balance He, with a total flow rate of 100 mL/min. The results suggests that the introduction of the VO_x sites increases the formaldehyde selectivity and decreases the dimethyl ether selectivity. The VO_x units in the primary Keggin structure were slightly more active than the surface VO_x species, and both VO_x sites were significantly more active than the MoO_x sites in the primary Keggin structure. Khadempir et al. synthesized pseudospherical palladium nanoparticles protected by PMo_{12} ²⁹⁰ at different pH or supported on graphene nanosheets (GNS)²⁹⁴ in acid solution. According to the results, Pd/ PMo_{12} /GNS demonstrates better poison tolerance as compared to the reference sample due to a superior ionic and electronic conductivity, small and highly dispersed nanoparticles. We have summarized recent works in the Table 8.

5. Conclusion and Future Challenges

Polyoxometallates (POMs) is a unique class of materials that have a broad range of potential forms and applications. Both their possible forms and their subsequent applications continue to be widely studied. In this review, we briefly described the history and progress of this class of materials with particular emphasis on energy-related applications.

The use of POMs in supercapacitors can offer significant opportunity to enhance the energy density of these devices by contributing pseudocapacitive charge storage effects in an efficient manner. This is a consequence of the high surface-to-bulk ratio of POMs, as well as their multiple redox states. POMs were shown to be suitable for improving performance in a variety of approaches to their use. These range from very simple addition of POMs to typical AC electrode pastes, to more complex methods of chemical linking to 2D materials and other emerging nanomaterials. However, because of their generally low electrical conductivity, the linking of POMs to an appropriate

conducting scaffold is particularly important and challenging, however progress is being made, for example, by using DFT simulation and prediction.

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For similar structure-property reasons as with SCs, these small cluster molecules offer the opportunity to improve the performance of battery technologies, and relatively speaking, this is being more widely explored. The poor electrical conductivity of pristine POMs and their typical high solubility in battery electrolytes results in a low cycling stability and poor rate performance when used as electrode materials. POMs-based composites can overcome these issues. Therefore, developing new POM-based composites is needed to expand the use of POMs in the field of rechargeable batteries as well as SCs. Particular attention could be given to POMOFs/carbon nanostructures, in which MOFs can mitigate the dissolution issue, while carbon nanostructures can increase the conductivity of POMs. More work focused on developing simple low-cost methods for the synthesis of POMOFs with high conductivity and controllable homogeneity, would be expected to improve their electrochemical performance in energy storage devices.

The energy storage mechanism for POMs-based electrode materials for rechargeable batteries and SCs are still not fully understood. The relatively high number of electron exchanges per molecule, when compared to other redox materials used in cathodic and anodic battery storage, complicate this. Therefore, detailed analysis is necessary to understand the reactions at the electrode/electrolyte interface. Advanced *in situ/operando* characterisation (microscopic and spectroscopic) and continued theoretical studies (such as by DFT) will likely be a necessary part of gaining an in-depth understanding of the reaction mechanisms and structural changes in POM-based electrodes, in order to promote further improvement in this field.

The interesting properties of POMs for energy storage are linked to the number of active sites in POM molecules, and these are also a critical property for catalysis. The application of POMs as catalysts is discussed for both water oxidation and ORR, as well as for other catalytic applications. Regarding water oxidation, the following three principles for the design of molecular WOCs recently outlined by Craig et al provide a strong point of reference for summarizing the topic:²⁹⁵ (1) Research

should focus on transition metal complexes which can undergo additional electron transfer steps by stabilizing high oxidation states, hence reducing the overpotential. (2) existing knowledge of heterogeneous catalysis, where DFT is used for material design, should be used to optimize the binding of the different reaction intermediates to the transition metal center. (3) electronic and steric effects of metal ligands should be investigated systematically. Advances in this field will allow the future implementation of ideal molecular WOCs into commercial electrolyzers with greatly enhanced selectivity, stability, and electron transport.

In the case of ORR catalysts, hybrid materials combining POMs with metal NPs, carbon-based materials and porphyrins have shown favorable performances. The synergies between POMs and the supports are crucial to improve the final composite stability and to achieve favorable ORR performances. On the other hand, pristine POMs with intrinsic catalytic activity towards ORR are scarce, and continuous efforts should be devoted to the discovery of cost-effective, efficient, and durable noble metal-free POM catalysts with good ORR performance. In general, the discussed examples demonstrate that the catalytic properties of POMs can be engineered finely to meet the requirements of different reactions. The molecular nature of POMs is enormously tunable and continues to present unique opportunities in the investigation of catalytic systems. Future research will focus on further advancements in POM design and immobilization, with special attention to the stability of the catalysts. The combination of POMs with metal NPs, carbon-based materials and other molecules has been shown to lead to favorable performance. In a synergistic fashion, these hybrid materials exhibit properties not accessible from the individual components. Furthermore, POMs have been shown to be useful for efficient production of hydrogen and for improved fuel cell performance.

In all three of the main energy-related contexts of applying POMs, one of the critical challenges that continues to be investigated is the anchoring of the materials to suitable substrates. POMs can very much be viewed as water-soluble oxyanions, just as can be found in the molecular pairing of many acid types. However, their relatively large molecular size also makes them true NP materials that present the opportunities mentioned in this review, when the particles are well dispersed

and fixed to a supporting scaffold. Amongst other methods, achieving this has been done through covalent and non-covalent approaches for carbonaceous and polymeric materials.

Despite this, there remains considerable room to improve knowledge in this area, and for it to be rationally guided, such as by DFT investigative work. Collaboration between theoretical modelers and experimental researchers will enable the discovery of new structures and new results in applications of POMs.

Together the outputs of theoretical investigations, advanced characterization work, and the synthesis and testing of novel POMs and POM composites can be expected to yield significant benefits. A deeper understanding of these materials and their structure and activity represents an accomplishment to advanced physical chemistry, given their complexity. While at the same time, their excellent activity and versatility make them exciting materials for applications such as in energy as we have discussed here. Overall, continued research into POMs for energy can be expected to make a significant contribution towards solving sustainable energy problems, at large.

Author contributions

D.P.D. and P.G.R. conceived the idea of the project. The energy storage part was written by M.H., S.A. and N.R.C. while A.S., S.G.F. and R.V.B. have contributed the energy conversion sections. All authors contributed equally to the preparation and reviewing manuscript.

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TOC: Polyoxometalates as anionic molecular metal oxides clusters with open frameworks and rich redox chemistry have outstanding versatility in energy conversion and storage research.

Figure 1 Keggin and Dawson POM structures including the acknowledged Keggin isomeric variations. Adapted with permission from Ref. ¹⁵, Copyright 2018, Macmillan Publishers Limited, part of Springer Nature.

Figure 2. Polyoxometalates molecules and their range of energy related applications for a cleaner environment.

Figure 3. (a, b) Cyclic voltammetry and charge/discharge curves for AC and AC/PMo₁₂ hybrid materials. Reprinted with the permission from Ref.¹⁸, copyright 2012, Elsevier. (c) Ragone plot demonstrating the high energy density of vanadium based POMs. Reproduced with the permission from Ref. ³⁶, copyright 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (d) The metallacalixarenes are able to anchor POM clusters inside the pockets of the material. Reprinted with the permission from Ref. ³⁶, copyright 2019, American Chemical Society.

Figure 4. (a, b) CV curves of PDDA, PMoW, RGO and the PMoW-PDDA-RGO composite at 10 mV s⁻¹. (d) Rate performances of RGO and the PMoW-PDDA-RGO composite determined from discharge curves. Reprinted with the permission from Ref.³³, copyright 2016, The Royal Society of Chemistry. (c) Schematic illustration of synthesis of W₂N@P doped CF using PW₁₂ as precursor with corresponding TEM and electrochemical analysis. Reprinted with the permission from Ref.⁶², Copyright 2018, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Figure 5 (a-c) SEM images of MnO₂ coated with different POMs such as PmO₁₂, PW₁₂ and SiW₁₂, respectively. Reprinted with permission from ⁶¹, Copyright 2018, American Chemical Society. (d) POM/PIL/graphene structure, where two POMs and one IL dimer (2[H₂PmO₁₂O₄₀][C₁₄H₂₄N₄]), are included in a periodic unit cell. (e) The calculated adsorption energies compared with those obtained for the H adsorptions on the same O sites of an isolated POM (H₂PmO₁₂O₄₀) on graphene. Reprinted with the permission from Ref.⁴⁵, copyright 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (f, g) Representation of anchoring of SiW₁₂@CNT where X denotes the functional groups -NH₂, -OH, -COH and -COOH, (f) Top(T), Bridge(B) and Hollow(H) points on the carbon network where the central axis of the SiW₁₂ cluster is projected. Reprinted with permission from ⁶⁴, Copyright 2018, Elsevier.

Figure 6 The ability of PMOs to discharge multiple electrons per molecule determines their outstanding ability to control redox processes in energy storage devices. (a) The reduction of all 12 Mo^{6+} to Mo^{4+} in $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ to form $[\text{PMo}_{12}\text{O}_{40}]^{27-}$, (b) Mo K-edge XANES spectra for PMo_{12} MCBs in the first discharging and second charging. (c) Schematic illustration of reaction mechanism for NAM during the discharge-charge process. Reproduced with the permission from Ref. ⁹⁰, Copyright 2012 American Chemical Society and Ref. ⁹¹, Copyright 2014, Elsevier.

Figure 7 (a) Scheme showing the charging process of $[V_{15}O_{36}(CO_3)]$ -based symmetrical LIBs (V^V centers; yellow, V^{IV} centers; teal), (b) Galvanostatic charge and discharge curves of $Li_7[V_{15}O_{36}(CO_3)]$ half-cell in within different voltage ranges at $100\ mA.g^{-1}$ (c) Cyclic stability of symmetric $Li_7[V_{15}O_{36}(CO_3)]$ device (d) the concept of electron/ion sponge in NPV anode. Reprinted with permission from⁹⁵, Copyright 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim and from ref. ⁹⁶, Copyright 2019 Elsevier.

Figure 8 (a) A possible interaction of lithium with POM/SWNT hybrid and TEM image of the POM/SWNT hybrid (b) schematic demonstration and TEM image of $\text{TBA}_3[\text{PMo}_{12}\text{O}_{40}]/\text{rGO}$ hybrid, (c) electrochemical performance of $\text{TBA}_3[\text{PMo}_{12}\text{O}_{40}]/\text{rGO}$ in Li-ion battery. Reproduced with the permission from ref. ⁸⁵, Copyright 2011, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim and from ref. ¹⁰³, Copyright 2014, Royal Society of Chemistry.

Figure 9 Charge storage mechanism in NMV cathode of (a) the molecular structure of $[\text{MnV}_{13}\text{O}_{38}]^{8-}$ and $[\text{MnV}_{13}\text{O}_{38}]^{20-}$ upon the insertion of Na^+ , (b) charge redistribution of $[\text{MnV}_{13}\text{O}_{38}]^{20-}$ analyzed by the charge difference, and (c) electron/ Na^+ ion sponge behavior. Reprinted with permission from ¹¹³, Copyright, 2017, American Chemical Society.

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Figure 10 Schematic of the structure of a redox flow battery. Reprinted with permission from ¹²⁸, Copyright 2011, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Figure 11 Catalytic cycles for the two primary reaction pathways proposed for the OER. Reproduced with permission from ¹³⁸.

Figure 12 a) Structure of Ru_4Si_2 , highlighting the central $[\text{Ru}_4(\text{O})_4(\text{OH})_2(\text{H}_2\text{O})_4]^{6+}$ core (ball-and-stick representation, Ru: blue, O: red, $\text{O}(\text{H}_2)$: orange. Hydrogen atoms omitted for clarity). The POM fragments are shown as gray polyhedra. Reproduced with permission from ¹⁴¹, Copyright 2008, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. b) Kinetics of O_2 formation (blue) and SA consumption (red) during light-induced catalytic water oxidation by Ru_4Si_2 5.0 μM using $\text{Ru}(\text{bpy})_3^{2+}$ 1 mM as the PS and $\text{S}_2\text{O}_8^{2-}$ 5 mM as SA in sodium phosphate buffer 20 mM (initial pH 7.2). Reproduced with permission from ¹⁴⁶

Figure 13 (a) Electrostatic capture of polyanion Ru_4Si_2 (red) by polycationic dendrons on the MWCNT surface (blue) and polyhedric structure showing the side and front view of Ru_4Si_2 with the $[\text{Ru}_4\text{O}_4]$ core in yellow. (b) General scheme for a water-splitting electrocatalytic cell with the integrated nanostructured O_2 -evolving anode. Reprinted with permission from ¹⁵⁹, Copyright 2010 Macmillan Publishers Limited.

Figure 14 (a) $\text{Co}_4\text{P}_2@\text{MOF-545}$ components: Co_4P_2 ($[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$); tetrakis(4-carboxyphenyl)porphyrin linker (TCCP-H_2); and Zr-based building blocks of the MOF ($[\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{OH})_2(\text{H}_2\text{O})_6]^{10+}$). The position of Co_4P_2 in the MOF channel was obtained from computations. WO_6 : green polyhedral, ZrO_8 : blue polyhedra or spheres, Co: cyan spheres, O: red spheres, C: gray, H: light gray, N: dark blue. (b) Kinetics of photocatalytic O_2 production over 0.5 mg of $\text{Co}_4\text{P}_2@\text{MOF-545}$ (blue), $\text{Co}_4\text{P}_2@\text{MOF-545}$ recycled once (red), twice (pink), and a solution containing PS porphyrin linker 131 μM and Co_4P_2 13 μM (green). Reaction conditions: $\text{S}_2\text{O}_8^{2-}$ 5 mM as SA in borate buffer 80 mM solution, pH 8, visible light ($\lambda > 420 \text{ nm}$, 280 W). (b) and (c) reprinted with permission from¹⁸³, Copyright 2018, American Chemical Society.

Figure 15 (a) Current density at +1.3 V (vs NHE) with a 44% Co₉-C electrode (black) and with Co₃O₄-C working electrodes at different Co contents (color lines). Labels indicate the total amount of Co in the blends. Reprinted with permission from ¹⁹⁷. Inset: Structure of Co₉, WO₆ (gray), PO₄ (black), Co (pink), P (black), O (red), reproduced with permission from ¹⁹⁵. (b) Linear sweep voltammetry (LSV) of Mn₁₆@graphene modified rotating ring-disk electrode in pH 7.5 phosphate buffer containing 1 M NaNO₃. The scan potential was from 0.3 V to 1.4 V at 50 mV/s on the disk electrode (blue line) and a constant potential of -0.35 V was applied to the ring electrode (green line). The bare graphene electrode was used as a reference under the same conditions (black and red lines). Inset: Structure of Mn₁₆, WO₆ (aqua), PO₄ (pink), SiO₄ (blue), Mn^{II} (yellow), Mn^{III} (brown), O (red). Reproduced with permission from ²²⁰, Copyright 2016, Royal Society of Chemistry.

Figure 16. Ball-and-stick and polyhedral representation of the polyoxoanion structures of compounds (a) Ni_{12} , (c) Ni_{13} and (d) Ni_{25} ; (b) Schematic view of the synthetic procedures. WO_6 , teal octahedra; PO_4 , pink tetrahedra; SiO_4 , orange tetrahedra; C, black sphere; O, red sphere; Ni, lime sphere. (e) Kinetics of O_2 evolution in the photocatalytic system at different concentrations of $\text{Ni}_{25} 3$. The symbols used to denote catalyst concentrations are $0 \mu\text{M}$ (black ■), $1 \mu\text{M}$ (red ●), $2 \mu\text{M}$ (royal blue ▲), $3 \mu\text{M}$ (teal blue ▼), $5 \mu\text{M}$ (magenta leftpointing triangle), and $10 \mu\text{M}$ (olive right-pointing triangle). Conditions: 300 W Xe lamp equipped with a long-pass filter (420 nm cutoff); 1.0 mM $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$, 5.0 mM $\text{Na}_2\text{S}_2\text{O}_8$, sodium borate buffer pH 9.0 (80 mM); total reaction volume 20 mL; vigorous stirring ($1.5 \times 10^3 \text{ rpm}$). Reproduced with permission from ²²⁴, Copyright 2015, American Chemical Society.

Figure 17 (a) Polyhedral presentation of the hematite surface with one Fe–OH reactive site highlighted in blue (two bound POM ligands and one $[\text{H}_3\text{I}^{\text{VII}}\text{O}_6]^{2-}$ SA drawn to scale). Reproduced with permission from ²³⁹, Copyright 2019, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Linear sweep voltammograms of Co₇(AlePyZn)₂/C and Pt/C in O₂-saturated 0.2 M NaH₂PO₄/NaOH (pH 7.4) and a scan rate of 10 mV/s. Reproduced with permission from ref ²⁵³, Inset: Structure of the polyanionic unit in Co₇(AlePyZn)₂, WO₆(blue), PO₄ (orange), Co (pink), P (orange), C (black), N (blue), O (red), and Zn (grey). Redrawn from ref ²⁴², Copyright 2015, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) Left: Structure of V₁₂, V (dark yellow), O (red), WO₆ (cyan), and PO₄ (blue). Right: Scheme of preparation of (PEI/V₁₂@Au⁰)_n LbL multilayer films on the ITO-coated electrodes (not scaled). . Reprinted with permission from ²⁵³, Copyright 2011, Elsevier.

Figure 18 (a) Kinetic current density (I_k) obtained from rotating disk electrode experiments normalized by the electrochemical surface area of the catalysts. Dashed line: Pd/POM-PDDA-MWCNT; solid line: commercial Pt/C catalysts; and dotted line: acid-treated MWCNT-supported Pd. Reproduced with permission from²⁵⁵. Inset: Representation of Pd⁰/POM-PDDA-MWCNT composite material. Reproduced with permission from²⁹⁶, Copyright, 2015, Royal Society of Chemistry. (b) Schematic representation of the synthesis of FeP/PMo₁₂-MWCNTs electrocatalysts. For simplicity, the axial ligands of FeP were omitted. Reproduced with permission from²⁶⁴, Copyright 2019, World Scientific Publishing Company (c) Electrochemical-reduction-assisted assembly procedure of the representative ternary Ag⁰NPs@POM-rGO nanohybrids. Adapted with permission from²⁶⁰, Copyright 2015, Royal Society of Chemistry.^{264 255 254}.

Figure 19 (a) NH_3 yield of various ZIF-67/POMs hybrids. (b) Energy levels and electron-transfer mechanism for ZIF-67 and POMs composite photocatalyst.²⁷⁴

Figure 20 Time-dependent product distribution in the $K_5[V_3W_3O_{19}]$ -catalyzed glucose conversion under (a) oxygen and (b) nitrogen atmospheres. Reaction conditions: 2 mmol of glucose, 0.167 mmol of $K_5[V_3W_3O_{19}]$, 10 g of water as solvent, 160 °C reaction temperature, 20 bar pressure, 1000 rpm stirrer speed, 0–5 h reaction time. With permission from ²⁷⁶

Figure 21 (a) Schematic illustration of the chemical-electric conversion (CEC) process. The anode is a simple graphite-felt electrode; the cathode is a gas-diffusion electrode loaded with the Pt black catalyst (4 mg cm⁻²). (b) Polarization curves of PMo₁₂ (0.3 mol l⁻¹) and biomass solution (fed with the anode side) preheated at 100 °C for 2 hours. The cathode side is pumped with 1 mol l⁻¹ H₃PO₄ solution. Figure adapted from ²⁷⁷

Table 1. POMs-based materials for lithium-ion batteries.

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Materials	Electrode	Initial discharge capacity (mAh.g ⁻¹)	Current /Current density /Rate	Capacity retention (%)	Cycle number	Ref.
K ₃ [PMo ₁₂ O ₄₀] (KPM)	Cathode	>200	50 μA	37.5	50@100 μA	2,89
TBA ₃ [PMo ₁₂ O ₄₀]	Cathode	260	1 mA	80.7	10	0
Na ₃ [AlMo ₆ O ₂₄ H ₆] (NAM)/KB	Cathode	437	0.04 C	91.2	50	91
(NH ₄) ₆ [NiMo ₉ O ₃₂] (ANM) NPs/KB	Cathode	490	17 mA.g ⁻¹	87.6	50	84
(KH) ₉ [PV ₁₄ O ₄₂] (KPV)	Cathode	370	100 μA	95	50	9
K ₇ [NiV ₁₃ O ₃₈] (KNiV)	Cathode	218.2	17 mA.g ⁻¹	~91.6	24	81
K ₇ [MnV ₁₃ O ₃₈] (KMV)	Cathode	300	17 mA.g ⁻¹	97.3	50	83
(NH ₄) ₇ [MnV ₁₃ O ₃₈] (AMV)NPs	Cathode	234	0.5 C	100	100	3
K ₉ [PV ₁₄ O ₄₂]/PP	Cathode	410	167 mA.g ⁻¹	90	50	94
Li ₇ [V ₁₅ O ₃₆ (CO ₃)]	Cathode	174	2 A.g ⁻¹	85	100	2
Na ₇ H ₂ [PV ₁₄ O ₄₂] (NPV)	Anode	961	100 mA.g ⁻¹	~57.2	150	6
TBA ₃ [PMo ₁₂ O ₄₀]/SW NTs	Cathode	~320	1mA	~96	10	85
SWCNTs/ Py-SiW ₁₁	Anode	1569.8	0.5 mA.cm ⁻²	37	100	98
CNTs/ SiW ₁₁ -NH ₂	Anode	1189	0.5 mA.cm ⁻²	54.6	100	6
PMO ₁₂ /PANI/MWNTs	Anode	1572	0.5 mA.cm ⁻²	63.6	100	99
SiW ₁₂ /rGO	Cathode	275	50 mA.g ⁻¹	~99.5	20	00
TBA ₃ [PMo ₁₂ O ₄₀]/rGO	Cathode	140	1 mA	~99	10	03
(EDA-rGO)/Anderson-type Na ₃ [AlMo ₆ O ₂₄ H ₆] (NAM)	Anode	1835	100 mA.g ⁻¹	~54.4	100	101

3D rGO@PANI/PW ₁₂	Cathode	235	200 mA.g ⁻¹	87	50	View Article Online DOI: 10.1039/D1003407J
Mo ₆ -SCN	Anode	1678	50 mA.g ⁻¹	52.2	100	97
(Py-Anderson) -CNTs	Anode	1898.5	0.5 mA.cm ⁻²	35.1	100	98
Mn-Anderson /SWNT	Anode	3405.4	0.5 mA.cm ⁻²	~27.4	100	99
TBA-PMO11/CNT	Anode	3014.1	0.5 mA.cm ⁻²	28.2	100	00
POMOF-based on (Ni ₆ PW ₉)SBUs	Anode	1421	1.25 C	~24.6	500	10
NNU-11	Anode	1322.3	50 mA.g ⁻¹	56.7	200	05
NENU-507	Anode	1008	100 mA.g ⁻¹	~63.5	100	07
POMOFs-based PMo ₁₀ V ₂ /rGO	Anode	2367.8	50 mA.g ⁻¹	45.4	100	08
POMs-ILs@MOFs	Anode	1665.5	0.1 A.g ⁻¹	~75	100	11
CuPW/SWNTs	Anode	1231.7	100 mA.g ⁻¹	71.8	170	106
PMo ₁₂ @FeBTC	Anode	1542.6	100 mA.g ⁻¹	42.6	50	01
Ni-POM	Anode	1325	100 mA.g ⁻¹	53.5	50	02
Ag NPs/POMs	Anode	1760	0.1 C	-	-	03
POM-derived metal composites as anode for Li-ion batteries						
Hierarchical MoS ₂	Anode	980	100 mA.g ⁻¹	97.6	50	04
MoO ₂ /Mo ₂ C/C spheres	Anode	1172	100 mA.g ⁻¹	~68.2	100	05
3D porous MoP@C hybrid	Anode	1439	100 mA.g ⁻¹	71.4	100	06
MoO ₂ @C nano- octahedrons	Anode	2936.8	100 mA.g ⁻¹	~49	50	07
Mo ₂ C/N-C mesoporous hetero- NWs	Anode	1206.2	0.1 A.g ⁻¹	78	50	08
3D hierarchically porous Mo ₂ C	Anode	1064.8	0.1 A.g ⁻¹	87	100	09
MoS ₂ -C	Anode	1375	1 A.g ⁻¹	90.9	200	10

MoO ₂ @MoS ₂ Nanoarchitectures	Anode	1259	100 mA.g ⁻¹	80.9	200	View Article Online DOI: 10.1039/D1EE03407J
MoC–N–C	Anode	2479	100 mA.g ⁻¹	50.2	300	12
2D layered mesoporous MoS _{1.12} Se _{0.88} /rGO	Anode	1238.4	100 mA.g ⁻¹	67	150	13
Red MoSe ₂ nanosheets	Anode	1706.88	1 A.g ⁻¹	65.9	500	14

Mo₆-SCN = [(Bu₄N)₂[Mo₆O₁₈-N-Ph-(o-CH₃)₂-p-SCN], NNU-11 = [PMo₈^VMo₄^{VI}O₃₇(OH)₃Zn₄][TPT]₅·2TPT·2H₂O (TPT=tris-(4-pyridyl)triazine), NENU-507 = (TBA)₃[PMo₈^VMo₄^{VI}O₃₈(OH)₂Zn₄(PBA)₂]·H₂O (TBA = tetrabutylammonium ion, H PBA = 4-(pyridin-4-yl) benzoic acid), CuPW = ([Cu₁₈(trz)₁₂Cl₃(H₂O)₂][PW₁₂O₄₀]), BTC = benzene-1,3,5-tricarboxylate, Ni-POM = [Ni₅(OH)₃(trzS)₃(en)(H₂O)(B-α-PW₉O₃₄)], Ag NPs/POMs = Silver nanoparticles/[Ni_{2.5}(Hpen)₄(PW₉O₃₄)]·5H₂O]

Table 2. Performance summary for POMs applied as ORR catalyst materials.View Article Online
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Catalyst	Medium	On set for ORR	Remarks	Ref
$\text{Co}_7(\text{AlPyZn})_2$	Neutral and basic	0.710 V (Neutral) and 0.75 V (Basic) vs RHE.	4 electron pathways of reaction.	242
$\text{NH}_4\text{Co}_7/\text{TTF-F}$ (i) $\text{Cu}_6\text{Ni}_7/\text{TTF-F}$ (ii)	Neutral	0.838 V vs RHE (i) 0.854 V vs RHE (ii)	One-step reduction of oxygen	243
$\text{Co}_4\text{P}_2@\text{Carbon}$ (SWCNT, Graphene flakes, N doped CNT)	Neutral	0.90V @N-CNT VS RHE	Out of various carbon support, the nitrogen doped CNT gives best performance.	244
$(\text{PEI}/\text{P}_5\text{W}_{30}\text{-RGO})_{10}$ multilayers	Acidic	0.80V vs Ag/AgCl electrode.	POM played main role in electrocatalysis	245
$\text{PMo}_{11}\text{V}@\text{carbon supports}$ (carbon-black, SWCNT and graphene)	Acidic	0.18 V vs. RHE $\text{PMo}_{11}\text{V}@\text{graphene}$ (best)	Strong dependency on carbon support.	246
$\text{PW}_{11}\text{-3DOM}$	Acidic	0.69 V vs. NHE	H_2O_2 Formation rate $2.4 \mu\text{mol h}^{-1}$	247

Table 3. Performance summary for co-catalyst POMs applied as ORR catalyst materials.

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Catalyst	Medium	Onset for ORR	Remarks	Ref
Pd/PMo ₁₂ /rGO	Acidic	0.6 V vs. Ag/AgCl	High methanol tolerance	256
Ag/PW ₁₂ /CNT	Basic	-0.4 V vs. SHE	Instability of POM in alkaline medium	257
Ag/PW ₁₂ /rGO	Basic	0.15 V vs. RHE	30% Ag NPs loading has comparable performance as commercial Pt/C catalyst with 20% loading.	258
Ag ⁰ NN@H ₇ [β-PMo ₄ ^V Mo ₈ ^{VI} O ₄₀]-GNS	Basic	+0.924 V vs. RHE	Green, facile and large-scale synthesis of nanohybrids.	259
Ag NPs@PW ₁₂ /rGO	Basic	0.86V vs RHE	20% loading of Ag NPs gives best performance.	260
Ag@Pt/MWCNTs-PW ₁₂	Acidic	0.85V vs. Ag/AgCl	25% of PW ₁₂ , 10% each loading of Ag and Pt NPs	261

Table 4. Summary of performance of Photocatalytic reduction of CO₂

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Catalyst	Final products yield			Remarks	Ref
	CO				
Ru ^{III} (H ₂ O)SiW ₁₁ O ₃₉] ⁵⁻	50 μmol			20-hour irradiation, Φ = 2%	315
H ₅ PWV ₂ W ₁₀ O ₄₀	0.9 μmol			The POM act as co-catalyst to a dirhenium molecular catalyst	316
Na ₁₀ [Co ₄ (H ₂ O) ₂ (PW ₉ O ₃₄) ₂ @g-C ₃ N ₄	107 μmol g ⁻¹ h ⁻¹			43 wt% Co ₄ content. Convenient recovery, steady reuse.	317
Catalyst	Product yield μmol g ⁻¹ h ⁻¹			Remarks	Ref
	CO	CH ₄	H ₂		
Au@[PTi ₂ W ₁₀ O ₄₀] ⁷⁻	12.8	2.1	2.6	Keggin-type POM	318
Au@[PW ₁₂ O ₄₀] ³⁻	0.5		0.15		
Au/K ₇ (PTi ₂ W ₁₀ O ₄₀)	2.1	0.35	0.29		
Catalyst	Final product μmol		TON	Remarks	Ref
	HCOOH				
[Mo ₁₅₄] ₁₁₆₅	116.7		778	POM microions, HCHO was also obtained.	319
[Mn ₆ P ₃ W ₂₄] ₉₃₁	40.6		270	No HCHO is produced	
[Mo ₁₃₂] ₁₀₆₄ @rGO	205		1366	HCHO was also obtained.	
Catalyst	Final product nmol/g		TON	Remarks	Ref
	CO	CH ₄			
NENU-605	52	170	135.9	TON of CH ₄ alone 104.1. TON here is per 1000	320
NENU-606	68	402	282.2	TON of CH ₄ alone 241.4. TON here is per 1000	
NENU-607	47	70	25.4	TON of CH ₄ alone 15.2. TON here is per 1000	

(NENU-605)-H[[Na₂K₄Mn₄(PO₄)(H₂O)₄]₃[[Mo₆O₁₂(OH)₃(HPO₄)₃(PO₄)₄][Mn₆(H₂O)₄]]

(NENU-606)-H[[Na₆CoMn₃(PO₄)(H₂O)₄]₃[[Mo₆O₁₂(OH)₃(HPO₄)₃(PO₄)₄][Co_{1.5}Mn_{4.5}]]

(NENU-607)-Mn [Mo₆O₁₂(OH)₃(HPO₄)₃(PO₄)₂

Table 5 Summary of performance of different POM-MOF catalysts.View Article Online
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Catalyst	E (V vs. SHE)	Onset Potential (V)	Current density (mA cm ⁻²)	Charge transfer resistance (Ω)	TOF (h ⁻¹)	Ref.
Co-PMOF	-0.8	-0.35	18.08	9.83	1656	291
Fe-PMOF	-0.7	-0.53	0.47	10.26	17.45	
Ni-PMOF	-0.8	-0.58	0.27	10.70	8.11	
Zn-PMOF	-0.9	-0.60	0.02	12.17	0.005	

Note: Charge transfer resistance was measured by electrochemical impedance spectroscopy (EIS).

Table 6. The performance of different electro-(photo)-catalyst towards NRR where STA- solar to ammonia. View Article Online
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Sample	NH ₃ yield	STA efficiency (%)	TOF (h ⁻¹)	Faradaic efficiency (% vs RHE)	Double layer Capacitance (mF cm ⁻²)	Ref.
ZIF-67	22.2 μmol/L ⁻¹ h ⁻¹	-	-	-	-	292
PMo ₁₂	15.8 μmol/L ⁻¹ h ⁻¹	-			-	
ZIF-67@ PMo ₁₂	39.4 μmol/L ⁻¹ h ⁻¹	0.008	24		-	292
PMo ₁₁ V	16 μmol/L ⁻¹ h ⁻¹	-	-		-	
ZIF-67@ PMo ₁₁ V	70 μmol/L ⁻¹ h ⁻¹	0.015	42		-	292
PMo ₁₀ V ₂	23 μmol/L ⁻¹ h ⁻¹	-	-		-	
ZIF-67@ PMo ₁₀ V ₂	74.8 μmol/L ⁻¹ h ⁻¹	0.016	42		-	
PMo ₉ V ₃	27 μmol/L ⁻¹ h ⁻¹	-	-		-	
ZIF-67@ PMo ₉ V ₃	134.6 μmol/L ⁻¹ h ⁻¹	0.029	76		-	
PMo ₄ V ₈	28.4 μmol/L ⁻¹ h ⁻¹	-	-		-	
ZIF-67@ PMo ₄ V ₈	149 μmol/L ⁻¹ h ⁻¹	0.032	94		-	
Fe _{1.89} Mo _{4.11} O ₇ /FeS ₂ @C	105.3 μg h ⁻¹ mgcat ⁻¹	-	-	54.7% at -0.4 V	3.5	293
FeMoO ₄ /FeS ₂ @C	51 μg h ⁻¹ mgcat ⁻¹	-	-	43.9% at -0.5 V	3.4	

Table 7. Yields of the main acids produced from the switchability experiments under oxygen and nitrogen atmosphere. Reaction conditions: 2 mmol of substrate, 0.5 mmol of (vanadium content) $\text{H}_6[\text{PV}_3\text{Mo}_9\text{O}_{40}]$ or $\text{K}_5[\text{V}_3\text{W}_3\text{O}_{19}]$ catalyst, 10 g of water as solvent, 160 °C reaction temperature, 20 bar oxygen pressure or nitrogen pressure, 1000 rpm stirrer speed, 1 h reaction time.

POM Type	Substrate	Environment	Yield	Ref.
$\text{K}_5[\text{V}_3\text{W}_3\text{O}_{19}]$	Glucose	Oxygen	YFA=20%	294
		Nitrogen	YLA=17%	
	Glyceraldehyde	Oxygen	YFA=16%	
		Nitrogen	YLA=17%	
$\text{H}_6[\text{PV}_3\text{Mo}_9\text{O}_{40}]$	Glucose	Oxygen	YFA=36%	
		Nitrogen	YLA=10%	
	Glyceraldehyde	Oxygen	YFA=42%	
		Nitrogen	YLA=40%	

Table 8. Literature overview of POM based materials for alcohol oxidation in direct alcoholView Article Online
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POM/composite	Electrolyte solution	Chronoamperometry			Ref.
		Voltage (V)	Intensity plateau/ (mA.mg ⁻¹)	Time (s)	
Pt/(epy) ₃ PMo ₁₂ O ₄₀ /rGO	0.5M CH ₃ OH + 0.5 M H ₂ SO ₄ N ₂ -saturated	0.7	118	3600	279
Pt/H ₃ PMo ₁₂ O ₄₀ /rGO	0.5M CH ₃ OH + 0.5 M H ₂ SO ₄ N ₂ -saturated	0.7	24	3600	279
Pd _{0.5} Ni _{0.5} /RGO/HPW-3	0.5 M CH ₃ CH ₂ OH + 0.5 M KOH	n.a.	~180	4000	321
Pt/H ₃ PMo ₁₂ O ₄₀ /GO/ Nickel foam 1	1 M CH ₃ OH + 0.1 M KOH	0.7	~50	7200	322
Pt/H ₃ PMo ₁₂ O ₄₀ /GO/ Nickel foam 2	1 M CH ₃ OH + 0.1 M KOH	0.7	~0	7200	322
Pt/H ₃ PMo ₁₂ O ₄₀ /GO/ Nickel foam 3	1 M CH ₃ OH + 0.1 M KOH	0.7	~0	7200	322
Pt/H ₃ PMo ₁₂ O ₄₀ /GO/ Nickel foam 4	1 M CH ₃ OH + 0.1 M KOH	0.7	~0	7200	322
Au@Pd/PMo ₁₂ /RGO	1 M CH ₃ OH + 1 M NaOH	-0.3	~4 mA.cm ⁻²	1000	323
Activated PdNPs@PMo ₁₂	1 M CH ₃ OH + 1.0 M NaOH	-0.2	~50	800	294
Non-Activated PdNPs@PMo ₁₂	1 M CH ₃ OH + 1.0 M NaOH	-0.2	~0	800	294
H ₅ PMo ₁₀ V ₂ O ₄₀ adsorbed on Pt	1 M CH ₃ OH + 0.5 M H ₂ SO ₄		<0.1 mA.cm ⁻²	1800	324
H ₅ PMo ₁₀ V ₂ O ₄₀	1 M CH ₃ OH + 0.5 M H ₂ SO ₄	0.3	<0.006 mA	1800	324
H ₃ PMo ₁₂ O ₄₀ Pt-Ru	1 M CH ₃ OH + 0.5 M H ₂ SO ₄	0.3	<0.04 mA	200	289
H ₃ PMo ₁₂ O ₄₀ Pt-Sn/C	1 M CH ₃ OH + 0.5 M H ₂ SO ₄	0.3	<0.4 mA	200	289
H ₃ PMo ₁₂ O ₄₀ Pt	1 M CH ₃ OH + 0.5 M H ₂ SO ₄	0.4	<0.003 mA	200	289
H ₃ PMo ₁₂ O ₄₀ Pt-Ru	1 M CH ₃ OH + 0.5 M H ₂ SO ₄	0.4	<0.154 mA	200	289
H ₃ PMo ₁₂ O ₄₀ Pt-Sn/C	1 M CH ₃ OH + 0.5 M H ₂ SO ₄	0.4	~0.4 mA	200	289
SiW ₁₂ O ₄₀ ⁴⁻ on Pt/C catalyst	1 M CH ₃ OH + 0.5 M H ₂ SO ₄	0.7	~1 A.mg ⁻¹ .cm ⁻²	1200	325
PtRu Nanoparticles with H ₃ PMo ₁₂ O ₄₀	1 M CH ₃ OH + 0.5 M H ₂ SO ₄	0.4	~0.8	3600	286
H ₃ PMo ₁₂ O ₄₀ PtRu/PDDA/MWCNT	1 M CH ₃ OH + 0.5 M H ₂ SO ₄	0.4	~1	3600	286
Pt black nanoparticles deposited onto TiO ₂ -supported Au-PMo ₁₂	0.5 M CH ₃ OH + 0.5 M H ₂ SO ₄	0.1	~0.2 mA.cm ⁻²	200	326
Pt black nanoparticles deposited onto TiO ₂ -supported Au-PMo ₁₂	0.5 M CH ₃ OH + 0.5 M H ₂ SO ₄	0.2	~0.65 mA.cm ⁻²	200	326

PtIr/PW ₁₂ /MWCNT	0.5 M CH ₃ OH + 0.5 M H ₂ SO ₄	0.6	200	3000	326
PtRu/C PW ₁₂	0.5 M CH ₃ OH + 0.5 M H ₂ SO ₄	0.5	~3 mA.cm ⁻²	1500	327
PMo ₁₂ /Pt ₄ Pd1/MWCNT	0.5 M CH ₃ OH + 0.5 M H ₂ SO ₄	0.6	200	3000	327
PdNPs@PMo ₁₂ -GCE	PBS (pH= 8.5) Phosphate buffer solution	-4.5	-0.5mA	300	290
PdNPs/PWO ₁₂ /ILs/GCE	0.5 M CH ₃ OH + 0.1 M HClO ₄	0.6	~0.045 mA.cm ⁻²	20000	328
Pt/PdNPs/PWO ₁₂ /ILs/GCE	0.5 M CH ₃ OH + 0.1 M HClO ₄	0.6	~0.050 mA.cm ⁻²	20000	328
Pt-PdNPs/NaPWO/GQD	0.5 M CH ₃ OH + 0.1 M HClO ₄	0.6	~0.045 mA.cm ⁻²	20000	329
PtNPs/NaPWO/GQD	0.5 M CH ₃ OH + 0.1 M HClO ₄	0.6	~0.035 mA.cm ⁻²	20000	329

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