

POLYOXOMETALATES: FROM INORGANIC CHEMISTRY TO MATERIALS SCIENCE

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1. ABSTRACT

Polyoxometalates have been traditionally the subject of study of molecular inorganic chemistry. Yet, these polynuclear molecules, reminiscent of oxide clusters, present a wide range of structures and with them ideal frameworks for the deployment of a plethora of useful magnetic, electroionic, catalytic, bioactive and photochemical properties. With this in mind, a new trend towards the application of these remarkable species in materials science is beginning to develop. In this review we analyze this trend and discuss two main lines of thought for the application of polyoxometalates as materials. On the one hand, there is their use as clusters with inherently useful properties on themselves, a line which has produced fundamental studies of their magnetic, electronic or photoelectrochemical properties and has shown these clusters as models for quantum-sized oxides. On the other hand, the encapsulation or integration of polyoxometalates into organic, polymeric or inorganic matrices or substrates opens a whole new field within the area of hybrid materials for harnessing the multifunctional properties of these versatile species in a wide variety of applications, ranging from catalysis to energy storage to biomedicine.

2. INTRODUCTION

Polyoxometalates have been known and used in the chemistry lab for nearly two hundred years, but only after the second half of the 20th century have we been able to fully perceive the richness of their chemistry, structure and activity. Modern techniques such as X-ray crystallography or NMR, and entire areas such as magnetochemistry or electrochemistry, have allowed a whole generation of contemporary chemists to build and make known a complete body of understanding on the structure, bonding and properties of these fascinating cluster molecules. Several enlightening reviews and compendiums have been published (1, 2, 3, 4).

With the turn of the century, the coming of age of materials science and the advent of nanotechnology, polyoxometalates are beginning to be considered as unique

chemical species that could turn from very special molecules to very useful materials.

With sizes just one order of magnitude smaller than the smallest of living biological structures such as the Rhinovirus (approx. 20 nm) they are not colloids but soluble polynuclear species. Indeed, one of the main reasons why polyoxometalates have not been considered in the past for the design of functional materials is precisely because their molecular nature makes them soluble in water and common organic solvents. Yet, they not only share structural and topological features with related transition metal oxides (1) but also resemble them concerning their redox, electron transfer or ion transport behavior. In all these respects, polyoxometalates can be generically considered as the perfect models for quantum-sized transition metal oxide nanoparticles (5, 6). For example, the electrochemical or photochemical injection of electrons in heteropolyanions (HPA) with the concomitant induction of thermally activated delocalization between metal centers and IVCT (Intervalence Charge Transfer Bands) leading to change in color, closely parallel the corresponding electrochromic properties of the corresponding oxides upon doping. On the other hand, POMs are ultimately dispersed species where most, if not all the metal centers that conform the cluster are not part of a bulk extended structure but are effectively located at *surface* sites, with all the implications this has concerning interfacial chemistry/electrochemistry and surface properties.

3. POLYOXOMETALATES AS MATERIALS

Contrary to ever-smaller nanostructures and quantum dots designed by means of physical methods following a top-down approach, polyoxometalates represent a very significant example of the bottom-up approach chemists use to build polynuclear and supramolecular structures with collective properties.

The control of size and structure in polyoxometalates is based on now well-known acid hydrolysis

and condensation reactions (1, 2), driven by the very rich acid–base chemistry of some transition metal cations, primarily W, Mo, and V. But this framework chemistry of isopolytungstates, molybdates and vanadates is remarkably broadened up when other elements come to add richness through structural and chemical multiplicity within the field of heteropolyanions. In addition, the remarkable stability of many of these clusters makes possible an extensive redox chemistry leading to a wealth of “blues”, reduced species, (2) where thermally-activated delocalization of electrons and a variety of spin states make for a remarkable landscape of electronic and magnetic states in small clusters that become in this way ideal models for the study of spin interactions (7-11).

Very recently, this rich oxygen-metal chemistry has been broadened with specific and unique examples that include for the first time anions such as S^{2-} or MeO^- (12, 13), or iron ions as the framework-building metals (13). The control of the extent of condensation and the isolation of new larger clusters formed through a building-block approach making use of smaller fragments to assemble larger units have also been a tremendous source of development in very recent years, especially for vanadium species (14, 15). At this point the field of polyoxometalate chemistry has broadened so much in variety of elements and structures, properties and applications that the reference books in the field would certainly welcome substantial additions and revision.

The intrinsic properties of polyoxometalates are of interest in themselves not only from a fundamental point of view but also to make of them materials of interest in various applications. Beyond their traditional interest as catalysts, polyoxometalates constitute base materials for electrochromics, energy storage and conversion devices (batteries, supercapacitors, fuel cells), sensors, or biomedical applications. Relevant to the latter is the newly tested insuline-mimetic effect of some of their derivatives or the composites formed between polyoxometalates and complex carbohydrates that allow their encapsulation and therefore their transport in biological systems (16). Also of interest are the recent studies on the mediated charge transfer in TiO_2 photochemical cells (17) and their use as electrolytes in acid fuel cells (18). Previously reported uses and tests are extensively reviewed in reference (4, 19).

On the other hand, many of the applications of polyoxometalate clusters as materials require their use in the form of membranes or electrodes, that is, in the form of solid, insoluble materials or coatings. There is therefore a main strategic line of work that has centered on the inclusion or integration of polyoxometalates in all sorts of substrates, polymeric, inorganic or mineral, and their combination with surfactants or organic carriers.

In this chapter we will try to show the basis for the applications of polyoxometalates in their own in materials science as well as the design of more complex materials and composites integrating them, with the recent development of hybrid organic-inorganic materials as a

general approach for the harnessing of polyoxometalate properties in solid polymeric functional materials.

Historically the use of polyoxometalate materials on their own has been limited to applications in which they could be dissolved (i.e. as homogeneous catalysts) or show specific changes in solution (for example through the formation of heteropolyblues). The isolation of these clusters in their solid state form has been more of a necessary step for their synthesis and purification. Indeed, during their synthesis, many different species coexist, from soluble molecular clusters to colloidal oxide particles (i.e. $H_3W_{12}O_{40}$ vs. $WO_3 \cdot nH_2O$). The former have been traditionally of interest to chemists whereas the latter are beginning to fall within the area of influence of physicists searching the nanoworld. In this way the complex supramolecular chemistry of tungsten or molybdenum polycondensates, relatively well understood but very poorly controlled in its details appears as a field of opportunities for interdisciplinary chemists willing to go into the field of nanomaterials with the asset of their bottom-up resources.

Molecular polyoxometalates have also been considered and discussed as perfect models for quantum size oxides, (5, 6) within a line of thought that tries to relate and connect molecular engineering, supramolecular chemistry (bottom-up approach) with ever-shrinking extended materials (top-down approach), an interface field in which fundamental issues such as the influence of size on the final properties of nanomaterials is crucial.

Also related to basic fundamental issues in nanoscience, polyoxometalates represent the boundary of the very different approaches that have been traditionally used to describe either extended solids or molecules. Band theory finds here a limit of a large but finite number of electronic levels in the valence region. On the other hand, simple models like the Ligand Field Theory, traditionally used to explain molecular magnetism also fail to account for the observed properties of these clusters. New features like diamagnetic ring-current effects in inorganic clusters are found for the first time (9). Fundamental new trends useful in understanding quantum confinement in oxide systems are developed, like a line of work dealing with magnetic studies of localized and itinerant unpaired electrons (8, 9, 10). And even unexpected surprises can be found in the way, like the molecular ferromagnetic interactions in a four-cobalt sandwich cluster (11).

In this way, polyoxometalates have contributed and are still bound to contribute to understanding a molecular world of chemistry much more complex than it could have been anticipated when they were first used as color-changing reagents in the 19th Century.

Indeed, for almost two centuries, the most useful properties and applications of polyoxometalates have been based on their rich acid-base and redox chemistries. A favorable acid–base chemistry that leads to a wealth of condensed anions, and the redox chemistry that those anions undergo, frequently with very small structural distortion. Upon reduction, polyoxometalates of Mo and W

(but not Vanadium) form mixed-valence species where the added electrons are delocalized. However, this is not a ground-state delocalization, but a thermally activated process similar to that found in extended doped oxide lattices. Again a correlation that makes of polyoxometalates excellent models for quantum-sized oxide systems and for their application as photo-electrochemical materials (5, 6).

It is now well established that polyoxometalates with octahedra sharing all corners but one (class II in Pope's classification) can be reduced reversibly to yield mixed-valent species usually known as *blues* or *browns*. The first stages of these reductions usually involve one-electron processes that introduce a delocalized electron throughout the structure (or most of it). The resulting unpaired electron is detected by means of an ESR signal corresponding to an unpaired spin with a *g* value near 2 (20). The thermal dependence of that ESR signal, and the appearance of hyperfine splitting at low temperatures show that electron localization occurs at low temperatures (ca. 60K for molybdates, 10 K for tungstates). Bulk susceptibility measurements on tungstates show a magnetic moment of $1.4 \mu_B$, (8, 10) typical of one W(V) ion with considerable spin-orbit coupling as expected from its location on the third row of the periodic table. No significant difference should be expected in this case with respect to a localized W (V) ion.

Two electron species, however, yield unexpected magnetic results that have been observed thanks to the use of a very sensitive method that allows the measurement of magnetic moments at room temperature by a ^1H NMR dipolar shift (9).

It is known that 2e- blues are diamagnetic, even at room temperature (2). These two electrons are not localized in a single W atom to yield W(IV). Instead, they are delocalized in the cluster (as shown by ^{183}W NMR) while occupying different W atoms at any given instant (as shown by XPS). A possible interpretation is the existence of a pair of delocalized W (V) ions so strongly coupled antiferromagnetically as to yield just a diamagnetic signal at room temperature. But a less conventional model could yield a better explanation as it will be discussed below.

Measurements of the magnetic moments of 2e⁻ blue species (by ^1H NMR Evans method using the parent oxidized compound as reference) show the existence of an excess diamagnetism that corresponds exactly to the one expected for two paired electrons in a cubic symmetry environment. Calculation of diamagnetism for a Keggin structure with cubic symmetry, using the classical Langevin's equation (with all quantum terms cancelled out because of the high symmetry) for the electrons circulating within a spherical surface of 5.4Å, leads to values in very good agreement with the experimental results. In turn that radius closely matches the average radius of a Keggin anion (5.5 Å). We can conclude that the electronic state of a two-electron blue may well be understood as a pair of correlated electrons delocalized within an extended "s-type molecular orbital". Breaking the cubic anion symmetry by substituting one or several of the metals in the cluster

decreases accordingly the excess diamagnetism observed, in agreement with the expected restriction in electron delocalization. (9) These experimental observations have found recently the counterpart in an independently proposed model for the electron delocalization as a form of "aromaticity" (21) that was suggested also in 1988 (9) Although the formalisms for the description of the symmetry of the electron delocalization pathways in solid state systems are different, this example represents a model at a nanometric level of what it may be happening in extended oxides. Furthermore, the behavior observed and described for these model clusters can provide an advance of what to expect when extended oxides are brought into the nanoworld by reducing their particle size following the bottom-down approach.

The electron delocalization, even of oxidized species was proposed as early as 1972 by Baker, Simmons and Wasfi (7). The evidence that the covalency existing in the cluster was affecting the magnetic properties was empirically present since the 70's. The study of reduced blue species containing paramagnetic ions corroborated the importance that the molecular bond has in describing the magnetic properties and therefore all electronic properties of the systems. Blue delocalized electrons can break the coupling between paramagnetic ions present in the structure or reinforce it, in a parallel way to that described in solid state physics by the RKKY model, or maybe even in the Kondo effect (8, 10, 22). Up to date, neither classical magnetochemistry, classical extended systems magnetism or no theoretical calculations have been able to predict or describe the observations of magnetic properties in odd or even electron blues, despite the intense efforts made.

Theoretical calculations have been performed in an attempt to derive a clear vision of the electronic structure of polyoxometalates. They were first based on extended Huckel methods, but more recently ab initio methods such as DFT have been performed specially on the Keggin structure (23-32). Using DFT based methods Poblet and co-workers have shown that the clathrate model where the inner anion XO_4^{n-} ion is encapsulated within a bent neutral $\text{M}_{12}\text{O}_{36}$ oxide network is useful to understand the electronic properties of oxidized and reduced Keggin anions. Calculations on 1e blues seem to agree well also with experimental results. However, calculations attempting to reproduce the electronic distribution of 2e-blues are just starting with limited success (25) understanding hopping as an equilibrium of forces, repulsion and delocalization of electrons, to stabilize a singlet ground state, and performing ab initio/multireference calculations on small 4 W fragments (26). Such equilibrium however can never justify the existence of a diamagnetic ground state at 10K, when the hopping does not exist.

In addition to the delocalized electron magnetism, new magnetic phases are being synthesized and new properties found. The measurement of the ferromagnetic coupling among Cobalt ions in Finke's (33) $\text{K}_{10}(\text{Co}_4\text{O}_{14}(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{27})_2) \cdot 22\text{H}_2\text{O}$ (11) was followed by the synthesis of new sandwiched compounds with a variety

of couplings among first row transition metals confined between polyoxometalate fragments. Although such confinement does not seem to participate from the whole polyoxometalate main framework structure, the resulting properties confined to a molecular level could very well find application in the near future in fields such as magnetism, electronics or medicine.

The most impressive example in terms of magnetism in clusters comes from the recently reported Keggin ion formed only with Fe as metal constituent, $(\text{Fe}_{13}\text{O}_4\text{F}_{24}(\text{OMe})_{12})^{5-}$ (13) even though the measured magnetic moment is smaller than the expected for the 13 Fe(III) atoms (expected 21.3 μ_B , measured 19.3 μ_B at room temperature).

Many new mixed-valent vanadium polyoxometalates with unusual structures, some giant, have been obtained in the last years (3, 14, 15). Even supramolecular structures formed by those giant polyoxometalates in forms that resemble vesicles have been reported very recently. All are based on vanadium and although they contain this metal in mixed valent state, there is not actual electron delocalization in the structure as is the case of “blues” of molybdenum and tungsten. No redox properties have been reported.

What we have discussed so far involve the intrinsic properties of clusters themselves. In that sense, there have been also some efforts to measure electronic and ionic transport properties of blue solids, with clear qualitative evidence that blues have some ionic but also bulk electronic conductivity (34).

3.1. Supported Polyoxometalates and Modified Surfaces

Despite the fascinating molecular chemistry of polyoxometalates, their application as materials requires, in most cases, their integration into solid systems or their adsorption on solid substrates. Thus, with the possible exception of homogeneous catalysis and their direct use in medicine, other applications based on electronic properties, redox reversible reactions and covalency in catalysis, electronic devices, coatings or anticorrosion protection, make always use of extended systems as support.

Polyoxometalates have been used as coatings on metals such as aluminum or silver. In the first case, there is a substantial decrease in the corrosion of aluminum. In the second it is clear that the polyoxometalate creates a barrier between silver and an electrolyte solution. In other cases, modified carbon electrodes have been obtained by coating the surface with polyoxometalates resulting in a marked decrease in the hydrogen overpotential for electrochemical water splitting. All those correlated effects on POM coatings are related with the ability of the anionic clusters to arrange themselves on surfaces and cover them completely. (35-38). In some cases, these arrangements allow the obtention of electrochromic devices (39) The progress on techniques such as STM and AFM have allowed the stochastic manipulation of polyoxometalates, one molecule at a time, as opposed to the statistical

manipulation of moles of molecules traditionally carried out in chemistry (3).

On the other hand, there are instances of self-assembled layers or modified electrodes where the identity of the actual material at work is not known. This could happen for instance after treatments too aggressive to retain the structure of the original cluster. One particular example is the formation of anticorrosive protection agents from polyoxometalates, where electronic techniques such as XANES or XPS have shown the existence of W(V) or Mo(V) and Mo(IV) when the starting polyoxometalate was a W(VI) or Mo(VI) species. In those cases, an oxide layer is assumed to be formed, that is very well adhered to the metal surface.

In addition to decorating surfaces, polyoxometalates can also be integrated into bulk solid materials in order to assure extended properties. One way to accomplish this is to crystallize polyoxometalates with inorganic or organic positive counterions to balance their negative charges yielding organized and insoluble supramolecular materials or hybrid inorganic-organic structures. Some initial examples were TTF-POM donor-acceptor complexes (40), and POM-adducts with conducting polymers which will be discussed below. More recently crown ether and surfactant- POM complexes have been prepared (41, 42).

POM can also be derivatized in the outer metal coordination sites leading in some cases to a three dimensional network. With the help of coordination complexes and organometallics new species have been reported to an extent beyond the scope of this review (4). Among all derivatized phases we want to remark those containing lanthanides as bridging units among inorganic heteropolyanion fragments that are the subject of intense studies for environmental applications dealing with sequestering of nuclear residues (43) and also as biocompatible inorganic species (44).

4. POLYOXOMETALATES IN HYBRID NANOCOMPOSITE MATERIALS

The field of hybrid materials is relatively young (45) but in the last two decades of development has suffered an explosive growth, both concerning new types of materials and novel applications (45-47). Within this booming field polyoxometalates are playing an increasingly important role (45).

Some of the earliest applications of polyoxometalates in general and heteropolyanions in particular were all those related with their catalytic activity, and they have indeed been used extensively as homogeneous oxidation catalysts. But in order to take advantage of some of the best characteristics of heterogeneous catalysts, there have been numerous works on supported polyoxometalates, in which the active molecule would get adsorbed decorating a particular substrate or supporting material. These substrate materials have ranged from conventional organic polymers to

inorganic mineral phases as it was advanced above, and the resulting POM-containing solids could be considered as an early stage in the development of materials integrating polyoxometalates as active species, albeit with a strong focus on their use as catalyst rather than as materials (47).

On the other hand, a more recent line of work has centered on the design of true materials to be used as solid electrolytes, as electrodes or even as magnetic, electronic or multifunctional materials that could harness the characteristic activities of POMs (45, 47). In these cases, the particular combination of active molecule and supporting matrix should be carefully chosen with each particular application in mind. For instance, when considering the design of polyoxometalate-based electrode materials, a particular kind of substrate polymer comes to mind, namely the large family of conducting organic polymers (COPs). Indeed, as we will see in the next pages, COPs provide an ideal network where polyoxoanions can be integrated, providing at the same time the electron (or hole) mobility necessary for electrocatalytic materials where both electronic and ionic conductivity are needed for a wide range of applications. On the other hand, the integration of POMs in polymeric matrices that are electrical insulators but which can provide or enhance the transport of ions or protons can lead to the natural design of electrolyte materials for a variety of solid state cells. Furthermore, the molecular magnetic properties of POMs can also be used in combination with conducting polymers to design novel hybrid materials.

4.1. Electroactive hybrids based on POMs and Conducting Organic Polymers

Like POMs, Conducting Organic Polymers (COPs) constitute another large family of compounds poorly known for more than a century, which were eventually understood and controlled only after the late 1970's and which are beginning to find commercial applications with the turn of the century. In addition to their peculiar conductivity, COPs feature reversible redox chemistry and ionic transport. Their electrochemically tunable doping states and their electrochromic and electrooptical properties, added to their low cost, light weight and processability, have made of COPs central materials in many different fields and applications.

But in addition to this development on their own, COPs are also an excellent basis for the design of the type of hybrid materials we are discussing here. They represent ideal constituents for the development of multifunctional hybrid organic-inorganic materials (45, 46) in which *either* of the characteristic properties of COPs *or their combinations* can be exploited to enhance or combine with those of polyoxometalates, providing at the same time the solid base. In this way, a large variety of functional hybrid materials can be designed and fabricated in which *multifunctionality* can be easily built to address specific technological needs.

We could find examples of hybrids with POMs and different types of conducting organic polymers, although most research work has focused on hybrids with polypyrrole (PPy), polyaniline (PAni) or polythiophene (PT) and their derivatives. This category

of hybrids spans a large number of materials and applications, including sensors or ion-selective membranes. Yet, our discussion will focus on the possible application of these hybrids in energy storage and conversion devices and we will analyze specifically the use of several types of hybrids as insertion electrodes in rechargeable lithium batteries, in electrochemical supercapacitors and in fuel cells.

The traditional hard-work method to introduce molecular inorganic species into a COP network relies upon the introduction of suitable coordination sites, groups or molecules which could lead to the formation of metal complexes. Those ligands or molecules can get incorporated to the polymer chain either through functionalization, by means of covalent bonds or by copolymerization with the usual monomers (47, 48). These methods would lead to strongly bonded (class II) hybrids. On the other hand, the introduction of molecular inorganic species into a COP network can also be accomplished by taking advantage of the doping process of the polymer leading to the incorporation of charge-balancing species into the structure, in which case class I hybrids are normally obtained.

The latter is the case for hybrid organic-inorganic materials with COPs and polyoxoanions, although the range of inorganic molecules that can be incorporated in this way is very large. Among the anionic species with transition metals that have been integrated into COPs we can mention tetrachloroferrate, hexacyanoferrate, and other cyano-metalate complexes, coordination compounds such as oxalatometalates, or EDTA complexes, tetrathiomolybdate as well as macrocyclic compounds like metal phthalocyanine or porphyrine, complexes (47).

However, among polynuclear metal complexes polyoxometalates have been by far the most widely studied (See (47) and references cited therein). As we have mentioned before, the electroactivity of these clusters parallels that of the corresponding oxides and it is this electroactivity which can be harnessed within the framework of polyoxometalate-containing hybrid materials for energy storage applications.

From a synthetic point of view, the preparation of Organic-Inorganic polyoxometalate-COP hybrids meets all necessary conditions for success. Namely, the strong oxidizing potential and acidic character of most polyoxometalates in their acidic form (i.e. heteropolyacids) are precisely the conditions required for the polymerization of monomers such as aniline, pyrrole or thiophene to yield the corresponding p-doped polymers. In this way, hybrid materials can be synthesized in which the bulky anions from heteropolyacids get trapped within the framework of the polymer formed (see Figure 2), leading to a material with all the unique properties of the conducting polymer plus the added activity of the entrapped inorganic cluster (47, 49-50).

Given the weak nature of O-I bonds in class I hybrids and the possible mobility of the inorganic molecules within the polymers, the question arises as to

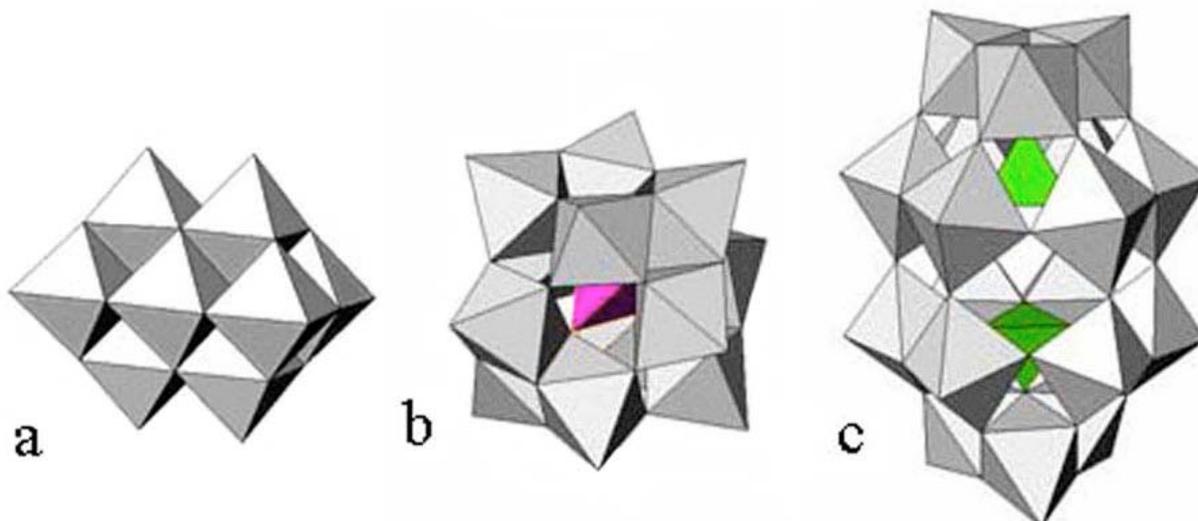


Figure 1. Polyhedral representation of isopolyanions (a) decavanadate ($V_{10}O_{28}^{6-}$) and heteropolyanions (b) Keggin anion ($PMo_{12}O_{40}^{3-}$) (c) Dawson structure ($P_2W_{18}O_{62}^{6-}$).

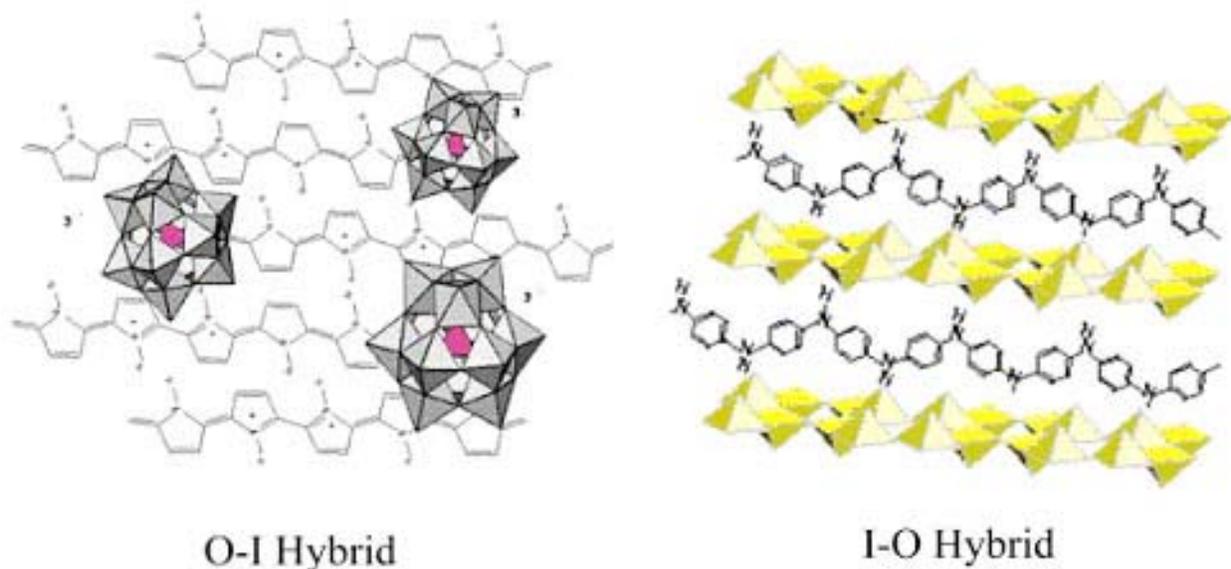


Figure 2. Two representative examples of the electroactive hybrid materials discussed here. Organic-Inorganic hybrids such as the polypyrrole-polyoxometalate on the left represent an interesting case of synergy since they allow the harnessing of the inorganic cluster electroactivity for energy storage applications, a function not possible without the polymer support. In Inorganic-Organic hybrids like polyaniline- V_2O_5 on the right it is the polymer which gets anchored within the inorganic lattice leading to hybrid materials with the combined electroactivity of both components.

whether the electroactive heteropolyanions incorporated to the polymer matrix will remain effectively anchored or will be expelled from the organic network upon redox cycling. This is an important point that goes beyond its basic interest and affects the use of COPs in a number of applications, including energy storage. This is so because common doping anions such as Cl^- or ClO_4^- usually found in p-doped polymers as charge-balance counterions, diffuse out of the COP upon reduction of the conjugated polymer. That deinsertion would simply correspond to the inverse process taking place during oxidative doping with insertion of anions. The processes of doping/undoping and charge compensation are not as straightforward as it might seem. It

has been shown (51) that even for COPs doped with simple anions, charge balancing during reduction can take place also by insertion of cations under certain conditions. Yet the important fact remains that simple doping anions get out of COP matrices upon reduction.

The possibility of anion deinsertion is obviously most significant in applications that require redox cycles of the hybrid materials, which include electrodes for rechargeable batteries and ultracapacitors but also electrocatalysts or sensors. This anion insertion-deinsertion mechanism has been shown to be detrimental for the application of COPs as active cathode materials in

rechargeable lithium batteries, since in combination with Li^+ -generating anodes they lead to a charge-reservoir situation in which the amount of electrolyte in the cell is a limiting factor and reduces the energy density of the system. (47, 50, 52-54).

In OI hybrids therefore, the challenge is to avoid the deinsertion of the active anion incorporated during the oxidation of the polymer. Large anions with high negative charge will have lower diffusion coefficients within the polymeric matrix and will be more likely to stay. This is the case for polyoxometalates, which have been shown to get effectively anchored within PANi, PPy, PT or even PAc matrices. The evidence for this anchoring is varied and has included cyclic voltammetry of the hybrids (49, 55) as well as quartz-crystal microbalance studies, (56-58).

The retention of large active anions in these hybrid materials has important consequences regarding their redox insertion mechanism. The permanence of the anions in the polymer matrix upon reduction forces the insertion of cations for the needed charge balance, with the inverse process of cation expulsion taking place upon reoxidation, thus converting p-doped polymers into cation-inserting redox materials. In addition to the above mentioned studies, direct evidence of this cation-based mechanism was obtained from analysis of lithium after discharge of a hybrid PANi-PMo12 electrode showing the incorporation of lithium ions corresponding well to the amount of charge involved in the redox reaction (50). The possibility of converting p-doped COPs into cation-inserting polymers opens new possibilities for their application, for example as selective membranes or sensors, or for their integration in energy storage devices such as electrochemical supercapacitors or rechargeable lithium batteries.

4.2. Energy-storage applications

Soon after the discovery of conducting organic polymers, their reversible electrochemistry, added to their light weight and polymeric nature made them very promising materials for application in thin, plastic energy storage devices like rechargeable lithium batteries. However, conducting polymers were not problem-free. Their effective capacity to store charge turned out to be relatively low and some of their characteristic properties turned into a handicap. For instance, as it was mentioned above, the anion intercalation-deintercalation taking place during cycling of p-doped COPs (the type used for cathodes) is detrimental to the energy density of a cell formed in combination with cation-generating lithium anodes (47, 52, 53). These limitations have been some of the major obstacles for the application of organic conducting polymers as lithium insertion cathodes making them to lose ground in favor of inorganic active materials in the race for achieving improved performance in rechargeable Li batteries.

The development of electroactive hybrid materials has been one of the major lines of work aiming at overcoming this problem and revamp the use of COPs in certain energy storage applications. Among hybrids, Inorganic-Organic (IO) hybrid materials were made with COPs (polyaniline,

polypyrrole, etc.) inserted into layered transition metal oxides or chalcogenides previously used as cathode materials (V_2O_5 , TiS_2 , MoO_3). For example, in reference (47), PPy-amorphous molybdenum sulfide, or PPy and manganese dioxide, either with MnO_2 particles dispersed in the polymer matrix or as a layered oxide have been reviewed. Hybrids with other unexpected oxides such as Fe_2O_3 have also been studied (59). In general, hybrid materials based on different forms of V_2O_5 with all sorts of conducting polymers have been some of the most widely studied for Li batteries and the topic has been reviewed elsewhere (47).

But in this chapter we will center on hybrids of the O-I type mentioned above, and in particular on the ones formed by polyoxometalates.

Examples of O-I hybrid materials that were initially targeted for battery applications include those based on COPs and heteropolyanions, and also hexacyanoferrate hybrids ($\text{Fe}(\text{CN})_6^{3-/4-}$) (47). The hybrid Polyaniline/ $\text{Fe}(\text{CN})_6^{3-/4-}$ has shown a very good performance in Lithium batteries. The mean discharge voltage of 3.2(3) Volts and the specific charge of 137Ah/Kg at a C/15 discharge rate yields a specific energy of 438Wh/Kg for the active cathode material. Cyclability of this material was very good both in discharges of 15 and 5 hours (60-61).

Hybrids based on POMs and conducting polymers were also tested as hybrid electrodes for rechargeable lithium batteries. In particular PMo12-PPy (49) and PMo12-PANi (50) hybrids were synthesized (both chemically and electrochemically) and tested. These tests were successful as proof of concept, that is, they showed the feasibility to use the clusters as charge reservoirs, and showed the conversion of the polymers from anion to cation (Li^+) insertion materials induced by the anchoring of the phosphomolybdate anion (50, 54). However, in our hands, the cells set up with these hybrid materials as cathodes coupled with metallic lithium anodes and using non-aqueous Li^+ electrolytes could not be used for repeated cycling. In the next section we will present though a remarkable example in which the same materials could be used under different conditions and media to store charge in a very efficient and reversible way.

In what follows we will discuss the possible use of POM-COPs hybrid materials in electrochemical supercapacitors. This option represents a different (and complementary) approach to batteries for the storage of charge, based on interfacial processes, and allows for higher power density but lower energy density than batteries.

Originally supercapacitors harnessed double-layer charge storage on the interface between microporous carbon materials and suitable electrolytes in a purely electrophysical capacitive mechanism, but more recently a new type of devices known as electrochemical supercapacitors are leading the way towards higher specific energy systems. These are based on redox active materials able to cycle repeatedly between two oxidation states and therefore represent an approximation between traditional supercapacitors and batteries.

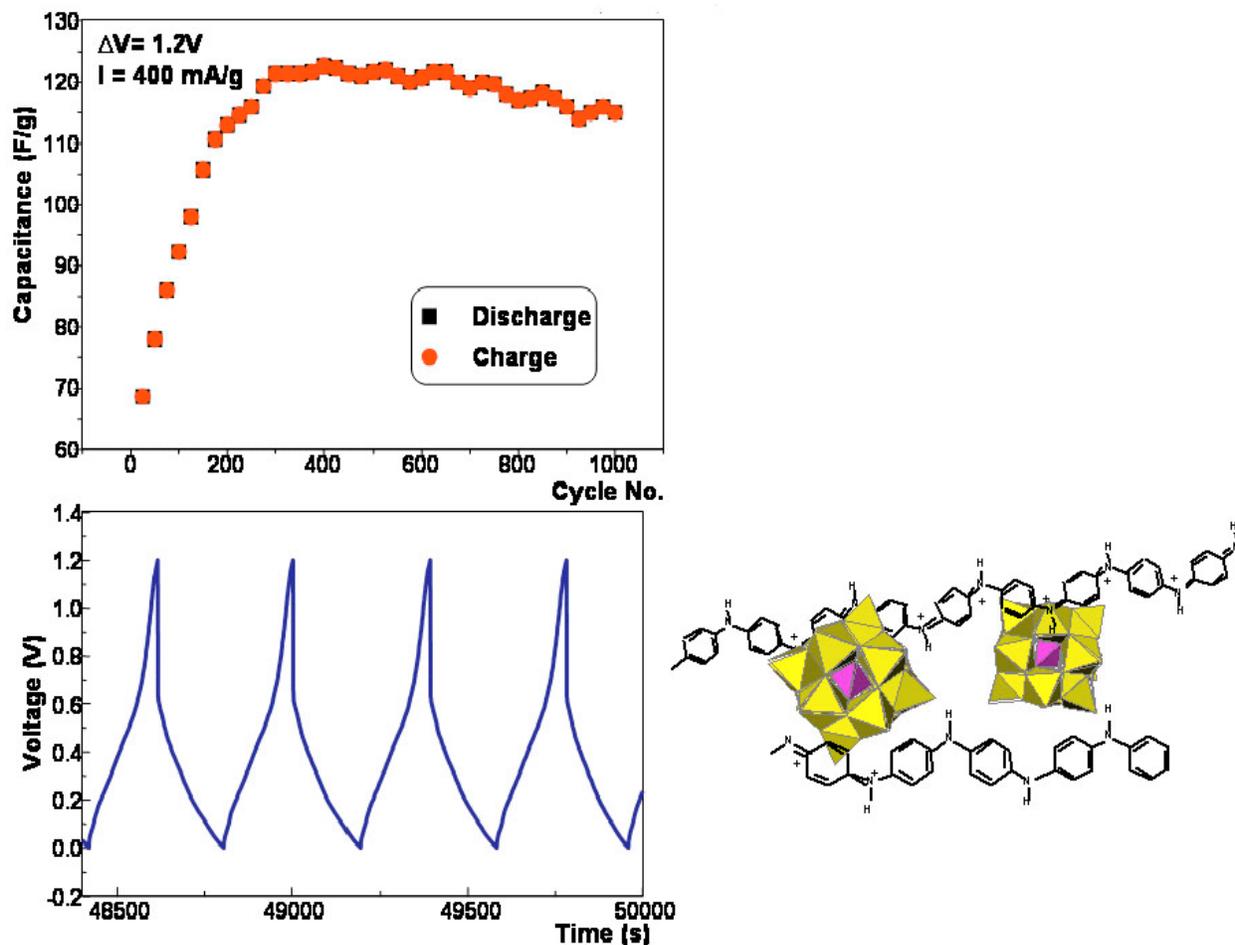


Figure 3. The hybrid PANi- $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (down) works in supercapacitor cells (bottom-left) keeping high capacitance values of 120F/g (under 400mA/g) for 10^3 cycles (left).

Conducting organic polymers, which can be p- or n-doped polymers, have also been proposed and studied as active materials for electrochemical supercapacitors. COPs as supercapacitor can deliver high specific power for a short period of time (10-100s), though with an energy density significantly lower than that of batteries (62).

The most desirable configuration for supercapacitors based on COPs is realized when the n-doped polymer is used as negative electrode and the p-doped polymer is applied as the positive electrode. This configuration is the most promising in terms of energy and power (62). Some reviews on application of COPs in supercapacitors have been recently published, among them are (62-66).

A few recent papers on the application of hybrid organic-inorganic materials as supercapacitors can be found in the literature. Hu, et. al reported the application of composite thin films formed by polyaniline and platinum microparticles (67). Polypyrrole/carbon nanotubes (68), where multiwalled carbon nanotubes are coated with polypyrrole, and the chemical polymerization of pyrrole

onto the surface of porous graphite (69-70) have also been reported.

Finally, we have recently pioneered the use of OI hybrids based on polyoxometalates and COPS in electrochemical supercapacitors (71-72) (Figure 3). Again, this application makes use of the reversible redox chemistry of both COPs and polyoxometalates, but contrary to their application in lithium batteries, where cyclability was very poor, these materials have shown very promising reversibility in symmetrical supercapacitor cells.

The reason for that could be found in the reduction mechanism of the heteropolyacids used in the design of these hybrids. POMs like the phosphomolybdic acid are known to suffer reversible reduction processes with a concomitant protonation, a mechanism which must be at work during cycling of the supercapacitor cells. Contrary to the behavior of these hybrids in non-aqueous Li^+ electrolytes, their use in electrochemical capacitor cells with acidic electrolyte membranes leads to a remarkable improvement in their cyclability behavior (see Figure 3) with preliminary

tests including up to four thousand charge-discharge cycles (72).

4.3. Electroionics

The energy-storage applications described above are but one of the many possible applications related to ionic and electronic transport in hybrids based on conducting polymers and electroactive molecules like POMs. As it has been mentioned above, in these materials coexist simultaneous electronic (or hole) conduction with ionic transport, and the anchoring of the large electroactive POMs leads to the conversion of the intercalation mechanism from anion- to cation-centered.

We propose the generic term “*electroionics*” for all processes and applications involving electron (or hole) conduction *coupled* with ionic transport. Under this general definition, many different applications like lithium batteries, electrochemical supercapacitors, sensors and actuators, or photoelectrochemical solar cells, could be properly considered electroionics. However, within the framework of this review we would like to call the attention to a particular application related to electro-ionic signal transduction, a field that will no doubt gain relevance for the development of myoelectric connections and neural-electronic interfaces. In this respect, electroionics could be built from hybrid materials in which conducting polymers with anchored polyanions of the type described above would help the translation between electronic signals and Na^+ or K^+ ions release or uptake. In this way, electroionics emerge as a prospective field in which much remains to be learned beyond our incipient understanding, an understanding which will eventually lead to control in the next few decades.

4.4. Polyoxometalates integrated in extended inorganic phases

In the previous sections we have discussed the integration of polyoxometalates in polymeric matrices, in particular in conducting polymers such as polyaniline or polypyrrole leading to the formation of hybrid organic-inorganic materials. But not only organic extended systems have been used to encapsulate polyoxoanions, the use of inorganic or mineral phases for the same purpose could lead to the development of what we could call Inorganic-Inorganic (I-I) hybrids, in the sense of combining pre-existing components both of which are inorganic in character. In this line of work there are already a few precedents, rooted in catalysis and intercalation chemistry. For example, Yun and Pinnavaia have been able to intercalate Keggin and Dawson anions and $(\text{Co}_4\text{O}_{14}(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{27})_2)$ into layered double hydroxides (73). And zeolites have also been tried as hosts for the “*in-situ*” formation and encapsulation of POMs for catalysis applications (74). In all these cases special care should be taken to make compatible the conditions (especially pH) for the synthesis and growth of both the POM and the host phase.

Finally, we could mention here a general approach recently followed (45) for the integration of

POMs into inorganic hosts, namely the use of sol-gel silica matrices. In this molecular engineering approach, a chosen polyoxometalate with any given property or added functionality can be used as a nano-building block to be integrated into the silica network. This could be accomplished either through strong covalent chemical bonding (as in Class II hybrids) or by simple trapping of the bulky cluster into the inorganic extended SiO_2 inorganic polymer. Taking into account that these silica networks can in turn be functionalized or modulated with suitable organic spacers, the structural possibilities and the range of properties available for design are multiplied.

To conclude, we can certainly forecast that the expansive multiplicity and richness of all the available matrices, whether organic or inorganic, in combination with the versatility inherent to polyoxometalates in themselves-both of which have been thoroughly analyzed and discussed throughout this review - will warranty a bright future for the development of materials with polyoxometalates as central active species, a field with a long tradition, presently in a resurgence stage and with a most promising future.

5. ACKNOWLEDGMENTS

The authors would like to acknowledge *partial* financial support from the Ministry of Science and Technology (Spain) (Grants MAT2001-1709-C04-01, MAT2002-04529-C03) and express his deepest gratitude for the *total* dedication of their Ph.D. Dedicated to Prof. Louis C.W. Baker (1921-2003), inspiring scientist and cherished friend students.

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Key Words: Polyoxometalates, Heteropolyacids, Heteropolyanions, Magnetism in oxide clusters, Heteropolyblues, Delocalized electrons, Redox, Electroactivity, Hybrid materials, Conducting polymers, Energy storage and conversion, Rechargeable lithium batteries, Electrochemical supercapacitors, Polyaniline, Polypyrrole, Review

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