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Hybrid nanocomposite materials for energy storage and conversion applications

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Functional Hybrid materials based on conducting polymers and inorganic photo-electroactive species provide a wealth of opportunities for the development of novel materials with improved properties. Polyoxometalates are one type of well-known inorganic species with most interesting photo-electrochemical activity. They are perfect models for nanometer-sized oxide quantum-dots both concerning structure, topology and electrochemical and photochemical properties. Yet, they have not been applied as materials because of their molecular nature (i.e., soluble in most solvents or electrolytes). In our group we have recently developed a research line dealing with the integration of these fascinating clusters in conducting polymer matrices to yield functional hybrid materials. Our past emphasis was on electroactivity for energy-storage applications but these materials can also be used, as it is shown here, for photoelectrochemical applications.

1. Introduction

Polyoxometalates are a large family of clusters with different but very well defined sizes and topologies formed by a predominant transition metal framework (usually W or Mo) and oxide anions to which a large variety of other elements can be incorporated. Several excellent reviews have been published on these remarkable cluster species [1–4].

With sizes just one order of magnitude smaller than the smallest of living biological structures such as the Rhinovirus (approx. 20 nm) polyoxometalates are not colloids but soluble polynuclear species (Fig. 1). 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 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.

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 to nanomaterials used by chemists to build polynuclear and supramolecular structures with collective properties.

The intrinsic properties of polyoxometalates are of interest in themselves not only from a fundamental point of view [7–9] but also to make of them materials of interest in various applications. Beyond their traditional interest as catalysts, polyoxometalates constitute potentially active materials for electrochromics, energy storage and conversion devices (batteries, supercapacitors, fuel cells), sensors, or biomedical applications. Also of interest are the recent studies on the mediated charge transfer in TiO_2 photochemical cells [10] and their use as electrolytes in acid fuel cells [11]. Previously reported uses and tests are extensively reviewed in reference [12].

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

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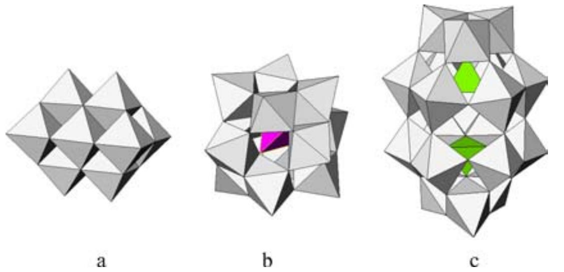

Figure 1 Polyhedral representation of (a) decavanadate $[V_{10}O_{28}]^{6-}$, (b) Keggin anion $[PMo_{12}O_{40}]^{3-}$, and (c) Dawson structure $[P_2W_{18}O_{62}]^{6-}$.

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.

We will discuss here the basis for the applications of polyoxometalates in their own as photoelectroactive materials 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.

2. Polyoxometalates as materials

Historically the use of polyoxometalate as materials on their own has been limited to applications in which they could be dissolved or show specific changes after dissolution. The isolation of these clusters in their solid state forms has been more of a necessary step in their synthesis and purification. In many instances, the solution is not clear to have contained dissolved anions or colloidal oxide particles (i.e., $H_3W_{12}O_{40}$ vs. $WO_3 \cdot nH_2O$). In any case, the applications are based on two main properties; the rich acid –base chemistry that leads to condensed anions, and the redox chemistry that those anions undergo with very small structural distortion.

When reduced, polyoxometalates of Mo and W (but not Vanadium) form mixed valence species (See Cyclic Voltammogram in Fig. 2) where the electrons are delocalized in a manner that is the counterpart of the thermally activated delocalization found in extended doped oxide lattices. This correlation in itself, which will be discussed in what follows, is what makes of polyoxometalates excellent models for quantum-sized oxide systems and for their application as photoelectrochemical materials. Furthermore, the existence of ring-current effects [13] and the correlations and magnetic interactions between added electrons within polyoxometalates [14, 15] add a great fundamental interest.

It is indeed well known that many polyoxometalates can be reduced reversibly to yield mixed-valent species usually known as blues or browns. This process can be accomplished either electrochemically or photochemically leading to characteristic broad Intervalence Charge Transfer bands centered in the near IR (see Fig. 3). The first stages of such reductions usually are one-electron processes that involve the existence of a delocalized electron throughout the structure (or most of it), associated to the detection of an ESR signal corresponding to an unpaired spin with a g value near 2 [16]. The thermal dependence of that ESR signal, and the appearance of hyperfine splitting at low temperatures show that electron localization occurs at low temperatures (60 K for molybdates, 10 K for tungstates). Bulk magnetic measurements on tungstates show a magnetic

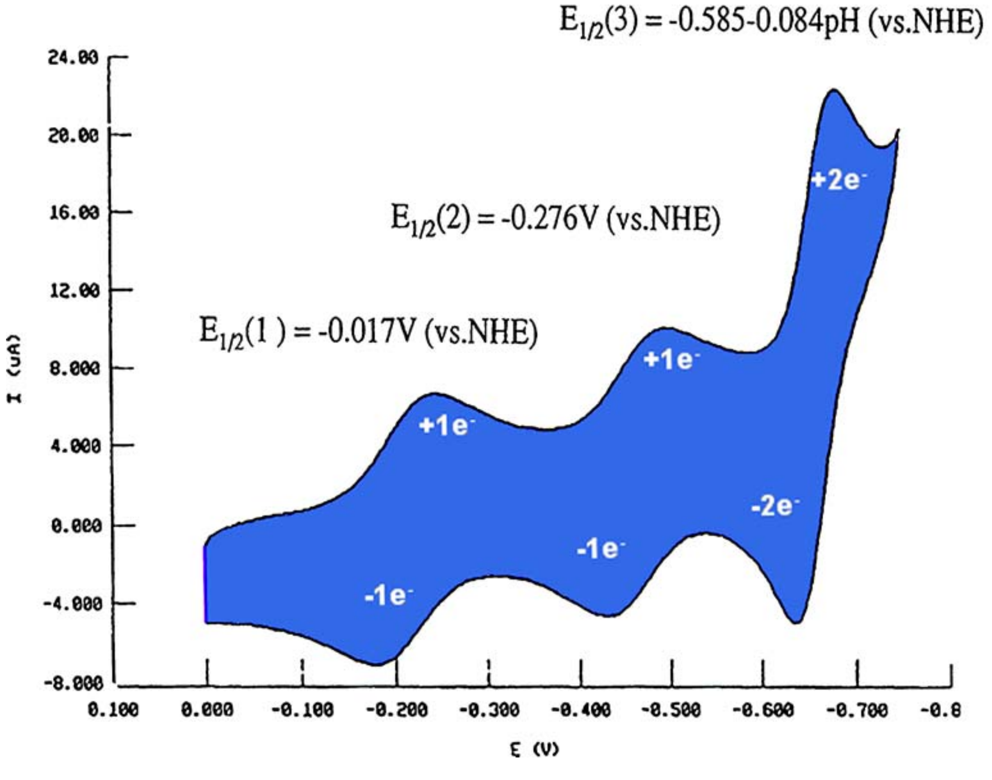

Figure 2 Cyclic voltammogram showing successive (and reversible) reduction processes for SiW12 polyoxometalate.

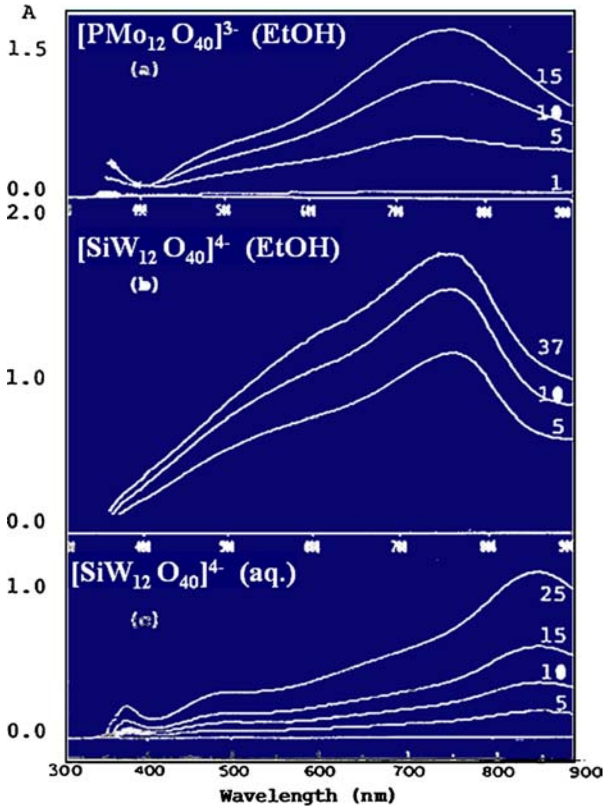

Figure 3 Intervalence Charge-Transfer Bands resulting from photochemical reduction of the clusters indicated in each case upon UV irradiation. These near-IR broad absorption bands are responsible of the darkening of polyoxometalates upon reduction.

moment of 1.4 μ_B, 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.

Fig. 1 shows some of the better know polyoxometalate structures, but the field is in continuous evolution and for instance, many new mixed-valent vanadium polyoxometalates with unusual structures, some of them giant, have been obtained in the last few years [3, 7, 8]. Even metastructures 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 no electron delocalization in the structure as detected and discussed above for "blues" of molybdenum and tungsten.

Polyoxometalates have been used as soluble molecular species in catalysis and biomedicine, in the form of coatings on metals such as aluminum or silver. Also, modified carbon electrodes have been prepared by coating the surface with polyoxometalates resulting in a marked decrease in the hydrogen overpotential for electrochemical water splitting. Also related to the use of polyoxometalates as nanomaterials we should mention a very significant emerging trend related to the recent progress in techniques such as STM and AFM which have allowed the stochastic manipulation of this type of large cluster anions instead of the statistical manipulation conventionally used in chemistry [3].

But polyoxometalates can also be crystallized or precipitated with inorganic or organic positive species that counterbalance their negative charges leading to solid molecular materials which can be purely inorganic adducts or hybrid inorganic-organic combinations. One of the most successful approaches in this sense has been the modification of conducting polymers with polyoxometalates to act as supported catalysts or the complete integration of the inorganic clusters within the framework of the polymers to form hybrid materials able to store energy in batteries or electrochemical supercapacitors. In the following section this application and novel photoelectrochemical applications will be discussed.

3. Polyoxometalates in hybrid nanocomposite materials

Some of the earliest applications of polyoxometalates in general and heteroplyanions in particular were all those related to 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 adsorb and decorate a particular substrate or supporting material. These substrate materials have ranged from conventional organic polymers to inorganic mineral phases 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.

On the other hand, a more recent line of work has centered on the design of true materials to be used as solid electrolytes or even electrodes that could harness the characteristic activities of POMs. 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 were polyoxoanions can be integrated, providing at the same time the electron (or hole) mobility necessary for electrodic 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.

4. 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 [17] 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 a polymeric base for a solid material. 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 [17–19].

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.

The introduction of molecular inorganic species into a COP network can be conveniently accomplished by taking advantage of the doping process of the polymer leading to the incorporation of charge-balancing species into the structure. This is the case for hybrid organic-inorganic materials with COPs and polyoxoanions.

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 Fig. 4), leading to a material with all the unique properties of the conducting polymer plus the added activity of the entrapped inorganic cluster [17, 20, 21] which remains effectively anchored within the polymer.

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 [17, 21].

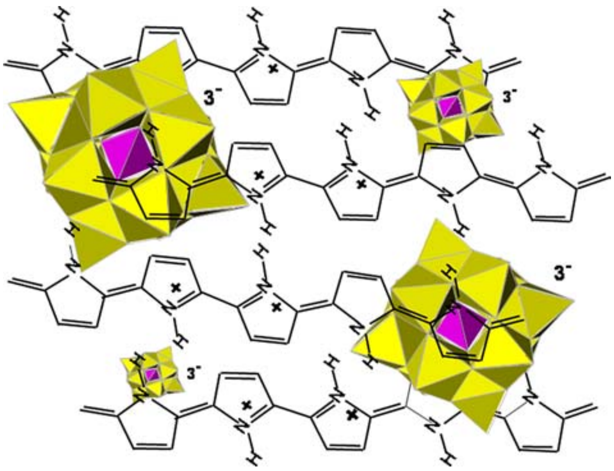

Figure 4 Schematic diagram of the structure of the hybrid Polypyrrole/PMo12.

4.1. 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 and conversion devices [22], such as rechargeable lithium batteries, or, more recently, electrochemical supercapacitors or organic solar cells. 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, 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 [17, 22]. 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 plastic Li batteries.

To overcome this problem and revamp the use of COPs in certain energy storage applications, new hybrid organic-inorganic materials were synthesized and studied. For example, within the group of molecular O-I hybrids we could highlight those based on COPs and heteropolyanions [20, 21], and also hexacyanoferrate hybrids $[Fe(CN)_6]^{+3-}$ [23].

Hybrids can also provide the added activity of the inorganic clusters in electrochemical supercapacitors. This option represents a different and complementary) approach to batteries for the storage of charge, based on interfacial processes, and allow 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 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.

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 (10–100 s), though with an energy density significantly lower than that of batteries [24].

The most desirable configuration for supercapacitors based on COPs is 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 [24].

Our hybrids composed of polyoxometalates and conducting polymers also are excellent materials for application in energy storage in electrochemical supercapacitors. This application makes use of the reversible redox chemistry of both COPs and polyoxometalates as it can be seen in the Cyclic Voltammogram in Fig. 5. The latter are known to suffer reversible reduction processes with a concomitant protonation, a mechanism which must be at work during cycling of the supercapacitor

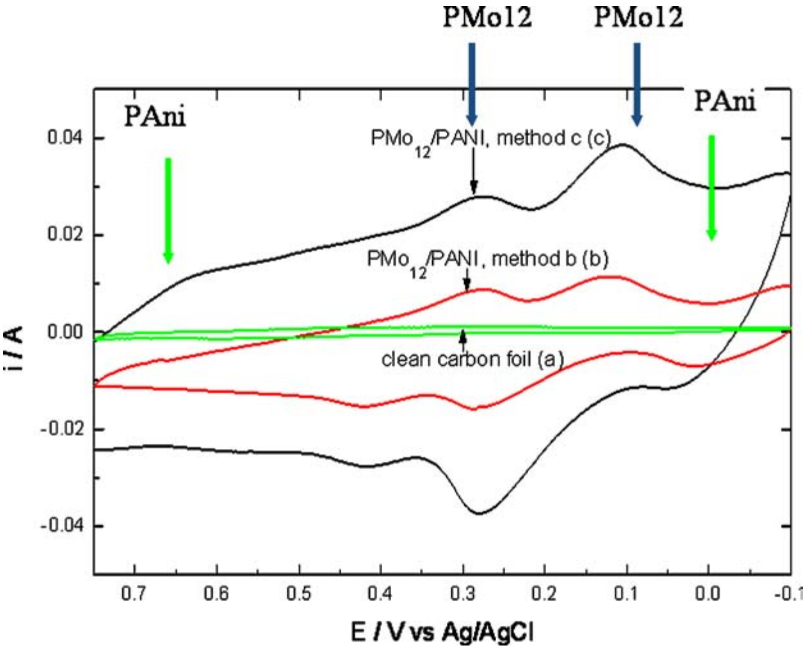

Figure 5 Cyclic voltammogram of the hybrid formed by Polyaniline and the phosphomolybdate cluster, where the activity of both components can be detected.

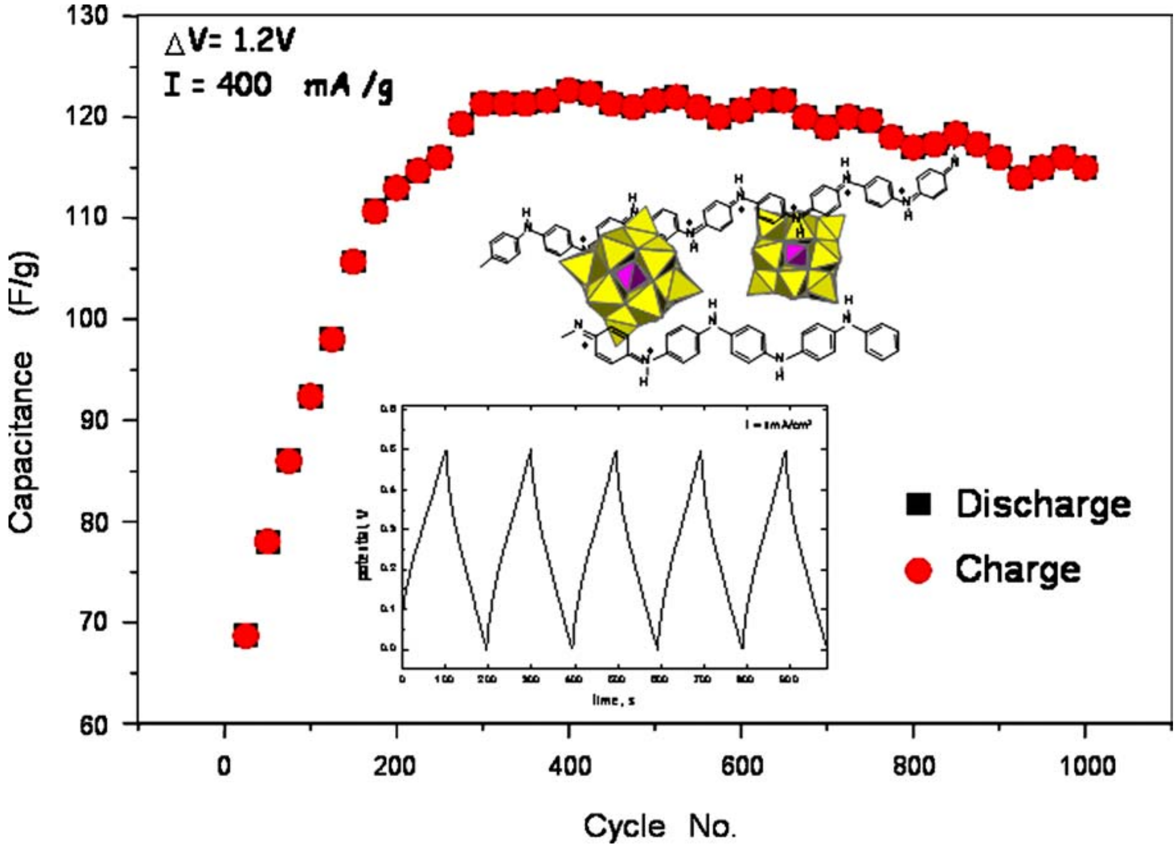

Figure 6 Charge-discharge cycles of an electrochemical capacitor cell based on the hybrid PAni-PMo12O40 (above).

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 Fig. 6) with preliminary tests including up to two thousand charge-discharge cycles and 120 F/g [25].

5. Conclusions

The development of hybrid materials based on Conducting Organic Polymers (COPs) represents an opportunity to improve upon the properties of these unique conjugated polymers and to develop new materials with new interesting properties.

The hybrid approach: In the case of energy storage applications, inorganic species contribute their added electroactivity to that of the COPs themselves in materials that keep their polymeric and conducting nature. In the particular case of OI hybrids, with molecular or cluster inorganics, the formation and redox cycling of the materials exemplify a peculiar synergic situation in which the activity of the molecular inorganic species can be harnessed in a practical electrode only because of their integration and anchoring within the polymer network.

In the same way that these polyoxometalate-containing hybrids have been used for energy storage applications, they could also be applied in energy conversion devices, where the photo-electrochemical activity of the clusters would be this time at work. Depending on the type of application it might be necessary to use dyes in order to absorb light in the visible region of the spectrum, similarly to the working mechanism of dye sensitized cells.

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References

1. L. C. W. BAKER, in "Advances in the Chemistry of the Coordination Compounds," edited by S. Kirschner (McMillan, New York, 1961) p. 604.
2. M. T. POPE, "Heteropoly and IsopolyOxometalates" (Springer Verlag, 1983).
3. M. T. POPE and A. MÚLLER (eds.), "Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity" (Kluwer Ac. Pub., Netherlands, 1994).
4. Chemical Reviews, special issue January/February 1998, all chapters.
5. P. GOMEZ-ROMERO and N. CASAN-PASTOR, *J. Phys. Chem.* **100** (1996) 12448.
6. P. GOMEZ-ROMERO, *Solid State Ionics* **101–103** (1997) 243.
7. A. MULLER, F. PETERS, M. T. POPE and D. GATTESCHI *Chem. Rev.* **98** (1998) 239 and references therein.
8. T. LIU, E. DIEMANN, H. LIU, A. W. M. DRESS and A. MULLER, *Nature* **426** (2003) 59.
9. K. NOMIYA, H. TORII, T. HASEGAWA, Y. NEMOTO, K. NOMBRA, K. HASHINO, M. UCHIDA, Y. NATO, K. SIMIZU and M. ODA, *J. Inorg. Biochem.* **86** (2001) 657.
10. R. R. OZER and J. L. FERRY , *Environ. Sci. Technol.* **35** (2001) 3242.
11. P. SAITI, S. HOCEVAR and N. GIORDANO, *Int. J. Hydrogen Energy* **22** (1997) 8009.
12. D. KATSOULIS, *Chem. Rev.* **98** (1998) 359.
13. M. KOZIK, N. CASAN-PASTOR, C. F. HAMMER and L. C. W. BAKER, *J. Am. Chem. Soc.* **110** (1988) 7697.
14. N. CASAÑ-PASTOR and L. C. W. BAKER, *ibid.* **114** (1992) 10384.
15. N. CASAN-PASTOR, J. BAS-SERRA, E. CORONADO, G. POURROY and L. C. W. BAKER, *ibid.*, **114** (1992) 10380.
16. C. SANCHEZ, J. LIVAGE. J.P. LAUNAY, M. FOURNIER and Y. JEANNIN, *ibid.* **104** (1982) 3194; id. **105** (1983) 6817.
17. P. GOMEZ-ROMERO, *Adv. Mater.* **13** (2001) 163.
18. P. GOMEZ-ROMERO and M. LIRA-CANTU, "Hybrid Nanocomposite Materials. Chapter for the Kirk-Othmer OnlineEncyclopedia of Chemical Technology," *Wiley-Interscience http://www.mrw.interscience.wiley.com/kirk/articles/hybdgome.a01/abstract.html* (2002).
19. P. GÓMEZ-ROMERO and C. SÜNCHEZ (eds.), in "Functional Hybrid Materials," ISBN 3-527-30484-3 (Wiley-VCH, Weinheim, 2004).
20. P. GOMEZ-ROMERO and M. LIRA-CANTU, *Adv. Mater.* **9** (1997) 144.
21. M. LIRA-CANTU and P. GOMEZ-ROMERO, *Chem. Mater.* **10** (1998) 698.
22. P. NOVAK, K. MUELLER, K. S. V. SANTHANAM and O. HAAS, *Chem. Rev.* **97** (1997) 207.
23. G. TORRES-GOMEZ, E. M. TEJADA-ROSALES and P. GOMEZ-ROMERO, *Chem. Mater.* **13** (2001) 3693; P. GOMEZ-ROMERO and G. TORRES-GOMEZ, *Adv. Mater* **12** (2000) 1454.
24. M. MASTRAGOSTINO, C. ARBIZZANI and F. SOAVI, *J. of Power Sources* **97/98** (2001) 812.
25. P. GOMEZ-ROMERO, M. CHOJAK, K. CUENTAS-GALLEGOS, J. A. ASENSIO, P. J. KULESZA, N. CASAN-PASTOR and M. LIRA-CANTU, *Electrochem. Com.* **5** (2003) 149.