**ADVANCED MATERIALS**

Hybrid Organic–Inorganic Materials—In Search of Synergic Activity**

By *Pedro Gomez-Romero**

This review surveys the work developed in the field of functional hybrid materials, especially those containing conducting organic polymers (COPs), in combination with a variety of inorganic species, from molecular to extended phases, including clusters and nano-sized inorganic particles. Depending on the dominating structural matrix, we distinguish and analyze organic–inorganic (OI) hybrids, nanocomposite materials, and inorganic–organic (IO) phases. These materials have been used in a wide variety of applications, including energy-storage applications, electrocatalysis, the harnessing of electrochromic and photoelectrochromic properties, application in display devices, photovoltaics, and novel energy-conversion systems, proton-pump electrodes, sensors, or chemiresistive detectors, which work as artificial "noses".
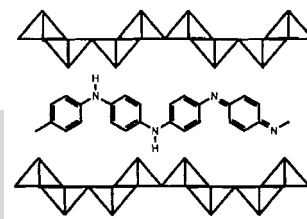
1. Introduction

The study of hybrid organic–inorganic materials is a recent but very fruitful and prolific enterprise. In addition to the early interest in structural hybrid materials based on carbon–silicon networks, many recent efforts have centered on the design of functional hybrid materials which harness the chemical activity of their components.

The hybrid approach is multifaceted. In some cases, conducting organic polymers (COPs) act just as a solid polymeric support for active species, whereas in other hybrid systems the activity of organic and inorganic species combine to reinforce or modify each other. But in every case the work on these hybrid materials involves the underlying use and sometimes even the explicit search for synergy.

Hybrid organic–inorganic materials in general represent the natural interface between two worlds of chemistry each with very significant contributions to the field of materials science, and each with characteristic properties that result in distinct advantages and limitations.

Research in the topic of hybrid materials entails challenges and opportunities. The main challenge is managing to synthesize hybrid combinations that keep or enhance the best properties of each of the components while eliminating or reducing their particular limitations. Undertaking this challenge provides an opportunity for developing new materials with synergic behavior leading to improved performance or to new useful properties. Indeed, hybrid materials frequently involve a combination of components that have been thoroughly studied in their respective fields but provide an additional dimension to their properties in becoming part of the hybrid compound.

Synergy might sound like a modern word, but it was used by the ancient Greeks and the concept it conveys is as old as human civilization. Indeed, among ancient materials we can even find a primitive precursor of hybrid composites with synergic properties. Adobe[1] is a mixture of clay and straw that serves as an effective structural composite material which has been used to make bricks and walls in arid regions throughout history. The addition of fibrous straw helps to prevent cracks, specially during the curing process, thus leading to a material with properties superior to the sum of the properties of its components; a synergic material.

Conventional, macroscopic composite materials such as adobe or reinforced concrete have shaped our world. Yet, when it comes to the microscopic world, reduced particle sizes boost the importance of the interphase in composite mixtures. And, as we move towards nanocomposite materials, where components interact at a molecular level, the concept of synergy takes on a new dimension, a chemical dimension.

The design of hybrid nanocomposites seeks to get the best out of two different chemical worlds, frequently with complementary strengths, to form new materials with new or improved properties. This approach has been successfully used in recent years in the design of hybrid polymers[2] with special emphasis on structural hybrid materials based on mixed sili-

[*] Dr. P. Gomez-Romero
Institut de Ciència de Materials de Barcelona
Campus UAB
E-08193 Bellaterra, Barcelona (Spain)
E-mail: pedro.gomez@icmab.es

con–carbon networks prepared by sol–gel methods[3–7] which can also entrap additional active species.[8] In this field the stakes are high and scientists aim at producing structural materials with properties between those of inorganic glasses and organic polymers.[3] But the expectations go beyond mechanical strength and thermal and chemical stability. These new materials are also sought for improved optical,[9–12] and electrical[13,14] properties, luminescence,[7,15–20] ionic conductivity,[21–23] and selectivity,[24–27] as well as chemical[28–30] or biochemical[31–33] activity.

Chemical activity is of core importance in functional materials. Sensors, selective membranes, all sorts of electrochemical devices, from actuators to batteries or supercapacitors, supported catalysts or photoelectrochemical energy conversion cells are some important devices based on functional materials. In this type of materials mechanical properties are secondary (though not unimportant) and the emphasis is on reactivity, reaction rates, reversibility or specificity. The hybrid approach can also be useful in this context by combining organic and inorganic species with complementary properties and reactivities.

There are a great variety of adducts that can be formed between organic and inorganic species. The first type to be systematically studied was the group of intercalation compounds.[34–37] The intercalation of small organic molecules into layered or channeled solids was initially studied from a basic point of view or in relation to possible selective reactivity within a variety of constraining inorganic phases.[36,38–40] Although these studies are important precedents in the field of organic inorganic compounds the resulting adducts were not designed nor used as materials. Nevertheless, in the last decade a growing number of hybrid systems have been prepared and studied with their application as functional materials in mind. When we consider the myriad of extended and molecular inorganic species, small organic molecules, and polymers available for the design of these hybrid materials it becomes clear that the variety of combinations is huge. The assortment would include innovative combinations, ranging from inorganic clusters,[41–43] fullerenes[44–48] or metal nanoparticles[49–51] dispersed in organic polymers to organic[52] and organometallic[53] molecules, biomolecules[30] or enzymes[31,52] dispersed in inorganic sol–gel polymers, or macrocycles[54–56]

or polyethylene oxide chains[57–62] intercalated into silicate minerals.

This review will center on a particularly fruitful and large group of hybrid functional materials. Namely, those containing COPs as components. This category alone accounts for a large number of materials and applications as it will be apparent below.

In the span of two decades, conducting organic polymers have enjoyed a dramatic transition from chemical curiosities to revolutionary new materials.[63,64] As such, they have received great attention and study in their own right.[65,66] Indeed, the field has boomed in such a way that recent reviews tend to center on particular polymers or applications.[67–71] Table 1 shows some of the polymers which will be discussed in this work.

Table 1. Schematic structures and chronology of relevant COPs.

Name	Label	Year [a]	Structure [b]
Polyacetylene	PAc	1977	
Poly(*p*-phenylene)	PPP	1979	
Poly(*p*-phenylenevinylene)	PPV	1979	
Polypyrrole	PPy	1979	
Polyaniline	PAni	1980	
Polythiophene	PT	1981	
Polyfurane	PF	1981	

[a] Year of the first report as conducting polymer. [b] Idealized linear structures. Protonation, conformational variability, and sometimes branching add complexity to these polymers.

The vast majority of reports dealing with COP materials involve the study of p-doped polymers, most frequently polypyrrole (PPy), polyaniline (PAni), or polythiophene (PT) and their derivatives. Among their properties and applications the most frequently studied are those related to their semiconductivity and electroactivity and range from their use as plastic conductors or light-emitting diodes (LEDs), to their use in energy storage applications.[70] Important as they are on their

Pedro Gomez-Romero obtained his B.Sc. in 1981 and M.Sc. in 1982 from the University of Valencia, Spain, and his Ph.D. in chemistry in 1987 from Georgetown University, Washington DC. He is currently a senior scientist at the Materials Science Institute of Barcelona (CSIC), where he leads a group working on functional hybrid materials, solid-state chemistry, electrochemistry, and materials for energy storage and conversion (i.e., rechargeable lithium batteries, fuel cells). In his spare time, popularizing science is Dr. Gomez-Romero's favorite creative activity and he has authored an award-winning book as well as several popular science articles both on the Internet (see http://www.geocities.com/sciencematters/) and in print.

own, the combination of COPs with a wide variety of available inorganic species with chemical, photochemical or electrochemical activity can lead to a wealth of hybrid functional materials some of which will be described in this review. Although not exhaustive, this account will try to show some of the possibilities brought about by this hybrid approach.

2. Classifications

The materials discussed can be classified according to several criteria. One of the most obvious is according to the type of application for which they are designed. But examining the chemical nature of a hybrid material we can identify criteria that will be more useful in recognizing common features and in understanding related behavior and properties. A classification of hybrids has been previously proposed according to the nature of the organic–inorganic interface, that is, according to the type of chemical interaction between the components:[5] Class I materials would be composed of "embedded" phases, forming hybrids where the interaction between organic and inorganic components is limited to weak bonds (ionic, hydrogen bonds or van der Waals interactions), and class II hybrids would be those materials where the organic and inorganic phases are linked together through strong chemical bonds (covalent, iono-covalent or coordination bonds). Although this is an oversimplified classification we will follow it here as a first approximation to the complex problem of sorting a wide variety of systems.

On the other hand, for the analysis and discussion of the functional hybrids considered here we will classify them into two major groups (and a category in between them) according to the nature of the host and guest phases. Thus, we will refer to organic–inorganic (OI) materials or compounds to denote hybrids where the organic phase is host to an inorganic guest, whereas inorganic–organic (IO) materials will be those with inorganic hosts and organic guests (Fig. 1). Obviously there will be cases falling right at the frontier between these two major classes, and we will also discuss these "nanocomposite" materials but that will be just a reminder of Nature's resistance to conform to our otherwise convenient classification schemes.

In addition to the above mentioned classification, Figure 1 reminds us that the inorganic species which will form our hybrid materials can be either molecular or extended in nature. This will have obvious implications in the nature of the hybrid compounds, a field in which the 10 Å molecular dimension, the 10^2 Å polymer chain dimension, and the 10^3 Å crystal grain dimension will need to be considered together.

In OI hybrids, the inorganic molecules will in general contribute their chemical activity and will need the structural support of COPs to become part of useful solid materials. In IO hybrids on the other hand, it will be the inorganic phase fulfilling the structural task although the inserted COPs can also imprint their polymeric nature onto the materials obtained. In between the two major groups of hybrids we will find nanocomposite materials where none of the phases dominates the
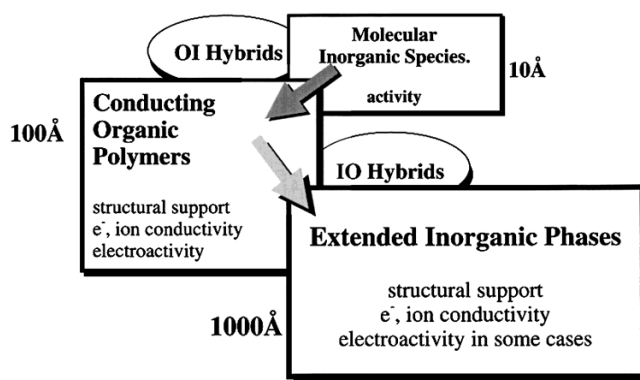

Fig. 1. Schematic representation of the three major groups of compounds considered in this work and their combinations to form OI and IO hybrids.

structure. And in all of these categories we will find and discuss examples of hybrids with useful combinations of properties and applications. For convenience and clarity, we will analyze below each major class of hybrids separately.

3. OI Materials

In this section we will describe and discuss hybrid functional materials with conducting organic polymers as the host or major component that incorporate inorganic species to form hybrids with the added functionality of the latter.

A major general way of introducing 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 be incorporated to the polymer chain either through functionalization, by means of covalent bonds or by copolymerization with the usual monomers. By definition, this approach leads to class II hybrids, with inorganic centers firmly attached to the polymer network. Deronzier and Moutet have recently reviewed this class of hybrids for PPy films.[72] This covalent link approach has been most extensively applied to PPy,[73–84] and also to PT.[85,86] It has also been used for PAni[87] but in this case a general application of the method is much restricted due to the high reactivity of the amino group.

Another general approach for the introduction of molecular species into a COP network takes advantage of the doping process itself. The doping of these polymers involves the introduction of holes (p-doped) or electrons (n-doped) into their conjugated chains. These processes take place with a concomitant incorporation of charge-balancing species into the structure, anions for p-doped and cations for n-doped materials. Hence the possibility of using active ionic species as dopants in the design of functional hybrids either by ionic exchange or by in-situ incorporation of the active species during the polymerization and doping process. Since p-doped COPs have been more widely studied, the literature abounds in active-anion doping used in place of, or in addition to, simple inert anions such as ClO_4^-, BF_4^-, SO_4^{2-}, etc. But of course

the same approach is feasible for the introduction of active cations into n-doped polymers.

This approach leads to less strongly bound inorganic species (i.e., class I hybrids) but has the advantage of a greater simplicity and versatility and has allowed the systematic preparation and study of hybrids containing a wide variety of anionic transition metal complexes such as tetrachloroferrate,[88–93] hexacyanoferrate,[94–109] and other cyano–metalate complexes,[110,111] coordination compounds such as oxalatometalates[112,113] or ethylenediamine tetraacetate (EDTA) complexes,[114,115] tetrathiomolybdate,[116–123] and macrocyclic compounds such as metal phthalocyanine[124–136] or porphyrin[137,138] complexes. Among polynuclear metal complexes polyoxometalates have been by far the most widely studied.[41,105,107,139–188] A number of examples of these oxide clusters have been used to modify or to be incorporated into polyacetylene,[130–133] PPy,[41,105,107,139–141,151,153,154,157,166,172,175,177,179,180,182,184] poly(*N*-methylpyrrole),[141,148,176,177] PAni,[107,142,143,150–153,155,156,159,160,162–165,169,173,179,180,182–188] and polythiophenes.[147,148,151–153,158]

Polyoxometalates are small oxide clusters whose size and solubility have caused them to be traditionally considered within the framework of molecular chemistry.[189–191] They are indeed complex molecules with several metallic ions coordinated by shared oxide ions, forming a highly symmetrical metal oxide cluster. Figure 2 shows two of the most common and extensively studied structures found for these clusters, the so-called Keggin structure conforming to the formula $[XM_{12}O_{40}]^{n-}$ and the Wells–Dawson structure $[X_2M_{18}O_{62}]^{n-}$. Polyoxometalates can in turn be classified as isopolyanions and heteropolyanions depending on whether they contain one or more kinds of atoms in addition to oxygen respectively. In the latter case one type of atoms is predominant, forming with oxygen the main framework of the structure. These so called addenda atoms are typically early transition metals such as W or Mo, and to a lesser extent V, Nb, or Ta.

The minor components of heteropolyanions are known as heteroatoms and they can be anything, from main group elements to transition metals to lanthanides[189] conferring an extraordinary chemical richness to this large family of polynuclear compounds. The number of addenda atoms in heteropolyanions is well defined for each species and varies typically from 12 to 48 with a corresponding increase in their size from a diameter of 10 Å for the Keggin structure (Fig. 2a) to ca. 25 Å, although larger clusters are known.[192] Polyoxometalates present therefore a state of aggregation that makes of them a natural link between the chemistry of extended oxides and the chemistry of monomeric molecules. Furthermore, their redox, electrochemical, and photochemical properties are also parallel to those of related oxides.[174,178] Heteropolyanions present very interesting molecular properties, from electrochemical activity,[189] electrochromism,[193] photoactivity,[194] magnetic[195,196] and catalytic properties,[197,198] which can be directly compared with those of related extended oxides.[174,178] Hybrid materials with integrated polyoxometalates would therefore allow the harnessing of these molecular properties putting them to work in applications previously

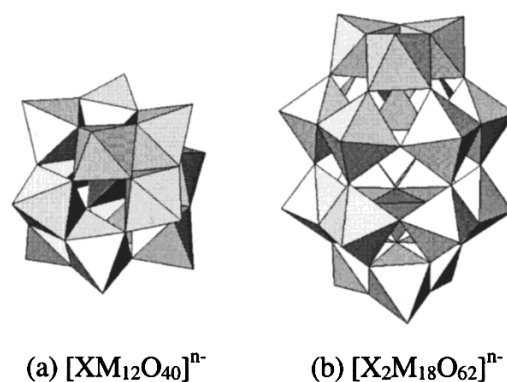**(a) $[XM_{12}O_{40}]^{n-}$**   **(b) $[X_2M_{18}O_{62}]^{n-}$**

Fig. 2. Structures of representative examples of polyoxometalates of the heteropolyanion type. a) Keggin structure $[XM_{12}O_{40}]^{n-}$. The phosphomolybdate anion presents this structure. b) Wells–Dawson structure $[X_2M_{18}O_{62}]^{n-}$.

unfeasible to this clusters due to their molecular nature and solubility. Their inclusion in conducting polymers yields hybrid materials with the processability and polymeric nature of the matrix and the added activity of the cluster. But, as for any other OI material with just ionic interactions between the polymer host and the inorganic guest, the permanence of the anions in the hybrid upon possible redox reactions is vital for the application of the hybrid as a useful material.

There are two major points concerning the nature of the insertion adducts formed between COPs and electroactive doping anions. One is the spatial distribution of the inorganic doping molecules and their concentration within the polymer matrix, the second relates to the reversible nature of the doping process.

The concentration and distribution of active inorganic species in OI hybrids can vary widely depending on the particular conditions of preparation. In principle, the amount of active anions incorporated to the hybrid is limited by the doping level attained for each particular polymer. But in addition, the presence of other (inactive) anions in the reaction or doping medium can decrease even further the amount of active species in the hybrid. On the other hand, it must be stressed that different applications will impose different requirements on the design of a particular material, its form and composition. Thus, OI hybrids used as supported catalysts might not require large bulk concentrations of active species but an increased concentration at the surface of the materials. Most of the earlier work conducted on polyoxometalate-doped COPs was aimed at the preparation of supported catalysts.[140,142,145–148,150,154,156,157,159,160,163,164,171,173,175–177,186,187] In those cases the concentration of polyoxometalates was secondary, counteranions such as ClO_4^- from the acidic medium or HSO_4^- resulting from the reaction of aniline with persulfate would compete with polyoxometalate anions in the doping of the polymers, reducing drastically the effective amount of the latter in the hybrids (see for example Hasik et al.[163] where overall ratios of aniline rings per heteropolyanion could vary from 400 to 10, the latter obtained only with large excesses of aniline and heteropolyanion with respect to persulfate). Nevertheless, in these cases the main goal was the preparation of

thin films and modified electrodes for electrocatalytically active interfaces. In this sense, Hasik et al.[159,163] examined the results of two possible ways of introducing heteropolyanions into PAni: by direct incorporation "in-situ" during the polymerization of aniline (i) and by acid–base doping of the previously polymerized PAni base (ii). They found the second, two-step method to yield a more active catalytic material thanks to the concentration of heteropoly anions at the surface due to their hindered diffusion. An example that stresses the importance of application-oriented choices concerning synthetic methods.

On the other hand, when a particular application requires bulk materials where the amount of active species is crucial, an optimal doping of the polymer must be sought to maximize the amount of anions incorporated, their distribution and the conductivity of the hybrid. Furthermore, in these cases care must be taken to avoid the presence of inactive anions which could compete for the doping of the polymers.[41,106,107,179,182,183,185] This is the case for instance in the application of OI hybrid materials for energy storage, where up to one molecule of phosphomolybdate anion ($[PMo_{12}O_{40}]^{3-}$) per nine aniline rings can be loaded into the corresponding hybrid[182,185] (compared with the maximum expected value of 1 $[PMo_{12}O_{40}]^{3-}$ per six aniline rings). In the hybrid of phosphomolybdate with PPy the maximum expected value of one $[PMo_{12}O_{40}]^{3-}$ per nine pyrrole rings was experimentally attained,[41,182] whereas in the case of hexacyanoferrate hybrids prepared also in the absence of other anions, up to one $[Fe(CN)_6]^{3-}$ anion per ten pyrrole rings was obtained[106] (close to the optimal expected value of 1 molecule per nine pyrrole rings).

A second important point concerning class I (loosely bound) OI hybrids, which is related to the reversible nature of the doping process, is the possibility of suffering the deinsertion of active species upon reduction of the conjugated polymer. This would simply correspond to the inverse process taking place during oxidative doping with insertion of anions (see Fig. 3a). This possibility is most apparent in applications that require redox cycles of the hybrid materials. These include most notably electrodes for rechargeable batteries and ultracapacitors but also electrocatalysts or sensors.
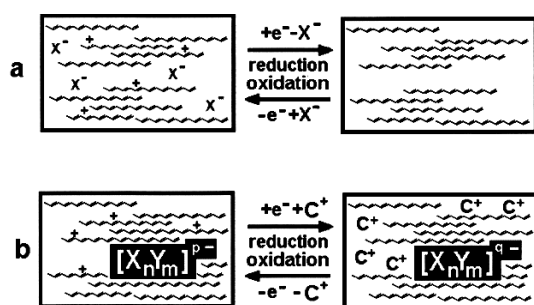

Fig. 3. Schematic diagram showing the redox insertion mechanisms of conventional COPs and hybrid materials. a) The typical mechanism for conventional COPs doped with simple small anions, which get inserted upon oxidation (p-doping) and de-inserted upon reduction. b) Modified mechanism achieved by anchoring large anions such as $[PMo_{12}O_{40}]^{3-}$. Reduction of the hybrid takes place with insertion of cations.

p-Doped COPs containing simple conventional anions such as ClO_4^- do actually suffer the deintercalation of those anions upon reduction. Nonetheless, the processes of doping/undoping and charge compensation are not as straightforward as it might seem. It has been shown[199] that even for COPs doped with simple anions, charge balancing during reduction can take place also by insertion of cations under certain conditions.

In OI hybrids though, the challenge is to avoid the de-insertion of the active anion incorporated during the oxidation of the polymer. Large anions with high negative charge will presumably 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 polyacetylene (PAc) matrices. The evidence for this anchoring is varied and has included cyclic voltammetry of the hybrids[41,142,182] as well as quartz-crystal microbalance studies.[169,175,186]

The retention of large active anions in these hybrid materials has important consequences regarding their redox insertion mechanism. As shown schematically in Figure 3b, 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 re-oxidation, 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–PMo_{12} electrode showing the incorporation of lithium ions corresponding well to the amount of charge involved in the redox reaction.[185] 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 rechargeable lithium batteries most commonly based on cation-producing anodes and a source–sink mechanism, which prevented the efficient use of conventional COPs due to their anion-insertion mechanism.[70,183,185,200]

Whereas bulky molecular clusters of the polyoxometalate type are easily anchored within COPs the question remains as to whether smaller active anions would also be. The electroactive hexacyanoferrate anion $[Fe(CN)_6]^{3-/4-}$ (HCF) and its hybrid with PPy provide an interesting example in this respect. Some experimental evidence suggested that the permanence or loss of HCF anions in PPy was potential dependent;[94] furthermore, cation incorporation into PPy–HCF hybrids has been reported to take place only when just the reduction of the HCF anion was involved, whereas the electrochemical reduction of the polymer (all in aqueous KNO_3) led to the de-insertion of hexacyanoferrate ions.[95,97] The nature of counterionic cations also plays a role in the redox behavior of HCF doped into PPy.[95,100] All these factors, which seem to complicate the redox chemistry and insertion/de-insertion properties of these hybrid materials can nevertheless be turned into useful behavior. Thus, films of PPy–HCF hybrids were used to demonstrate the feasibility of

REVIEW

switching between a strongly bound state for HCF in the polymer to the release of controlled amounts of the anion by cathodic current pulses in what could be considered a model for drug-release chemical systems.[95]

The electrolyte solvent is another important factor to take into account when considering the possible anchoring of HCF in conducting polymers. A study conducted on PPy materials showed that diffusion coefficients of anions in PPy (I⁻, Cl⁻, and $[Fe(CN)_6]^{4-}$ were studied) are strongly dependent on the solvent due to the different solvation and swelling of the polymer in each case.[98] Concerning specifically the anchoring of HCF, it has been found that repeated redox cycling of PPy–HCF hybrids results in HCF de-insertion when aqueous electrolytes are used, whereas the use of certain organic solvents for the electrolyte allow for the retention of the anion and consequent insertion of cations for balancing the charge during the reduction process as shown in Figure 3b. This feature has allowed the use of PPy–HCF[103,107,108] and also PAni–HCF[109] as active cathode materials in reversible lithium cells, where non-aqueous solvents are commonly used.

To finish the discussion on HCF-based hybrids, it might be worth mentioning the remarkable bias towards PPy compounds. A large number of papers have appeared over the last twenty years dealing with many aspects of the synthesis and electrochemistry of PPy–HCF hybrids,[94–108] an effort apparently unmatched for PAni or PT hybrids. Ease of preparation might be at the heart of this bias but it should be stressed that other COPs offer different properties and therefore the opportunity to produce tailor-made materials for specific applications. In our own experience for instance, the move from PPy–HCF materials[106,108] into the uncharted PAni–HCF[109] involved certain changes in our synthetic approach, but the preparation of the PAni–HCF hybrid was eventually optimized and simplified and led to a material much superior to the PPy derivative as a cathode for reversible Li cells.[109]

We have seen examples of how to take advantage of the doping process in COPs in order to anchor large or even medium-sized active anions into their networks. But in principle the "active-anion" doping approach seems obviously limited to anionic molecules when dealing with the most common p-doped COPs. However there are several ways to overcome this expected limitation. A suitable substitution of neutral ligands with anionic functional groups for example can turn neutral or even cationic complexes into anions. Thus, sulfonated ligands were used for instance for the integration of the metal phthalocyanine complexes mentioned above or iron trisphenantroline sulphonic acid complexes[201] into COPs.

In addition to the doping species, the polymers themselves can also be derivatized by sulfonation[202] or substitution with other anionic groups such as alkylcarboxylic acids.[203] This "self-doping" approach also leads to cation-inserting materials. In the above examples the applications in mind were cathodes for lithium batteries[202] and proton-pump electrodes,[203] respectively.

Another way to introduce cationic species into p-doped COPs is the previous doping of the COPs with anionic organic

polyelectrolytes which—similarly to the inorganic polyoxometalates described above—have a hindered diffusion out of the matrix.[204,205]

4. Nanoparticles Dispersed in Conducting Organic Polymers. Hybrid Nanocomposites

As mentioned in the introduction, some hybrid materials defy normal classification. While most compounds can be reasonably considered to be formed by a predominant matrix (be it organic or inorganic) and a host component inserted within the structure of the former, that is not the case for certain types of hybrids. Nanocomposite materials, formed by colloidal nanometer-sized particles of metals or metallic compounds dispersed in COPs constitute a good example and a whole category in themselves, which has been the object of a recent review.[206] In these materials, inorganic nanoparticles are not the host for the intercalation of organic polymers, but at the same time they are too large to be considered guest species conforming to the structure of the polymers. These materials could therefore be considered as true composite materials where each component still retains its own structure but with an increased interfacial interaction derived from the small particle size.

Within this category a first group of materials is formed by nanosized metal particles dispersed in COPs.[49–51,207–211] Most frequently the metals used are precious metals from group 10, Pd and Pt, and the hybrids are designed for catalytic purposes, such as proton and oxygen reduction,[49,207,208] hydrogen oxidation[49] as well as hydrogenation reactions.[50] Although metals are the most common elements dispersed within COPs, there have also been interesting studies on dispersions of other active elements such as carbon[211–217] or sulfur[218] for use in energy-storage devices,[212,213,218] as electrocatalysts for environmental remediation in Cr^{VI} reduction,[175,211] or as sensors and "artificial noses".[216,217]

A second group of materials is constituted by those in which the nanodispersed phase is an oxide. Several hybrid materials based on colloidal particles of transition metal oxides (γ-Fe_2O_3,[219,220] MnO_2,[221–223] CuO,[224] TiO_2[225–229] and WO_3[230–234]) as well as tin oxide[235–237] and silica[13,235,237] have been reported. In addition to the more extensively studied work on oxides, recent reports have extended this family of hybrid composites to other colloidal semiconducting particles such as CdS,[42,225,227,238–243] CdSe,[42,238,239,243] and copper or silver halides.[242]

5. IO Materials

Despite their relatively large molecular weights, conducting organic polymers can in certain cases play the role of intercalated guest molecules inserted within van der Waals gaps of layered or channel inorganic phases. At least in principle, in these cases the structure of the inorganic guest dominates the

structure of the hybrid and the polymers adapt to it. A true host–guest association would imply nonetheless that the organic molecule could leave the inorganic structure reversibly, which is normally not the case for the materials described below. Indeed, the key to the preparation of many of these IO hybrid materials rely upon in-situ polymerization of the corresponding monomers once intercalated into the inorganic host or alternatively on the simultaneous formation of both organic and inorganic polymeric structures. Otherwise, the long chains and large molecular weights of the frequently insoluble COPs would prevent their effective diffusion into the host structure. Nevertheless, despite the irreversible character of the process, the inclusion of COPs within the structure of extended solid phases leads in many cases to remarkable hybrid materials with synergic properties. Examples of this type of IO hybrid materials include insertion compounds of COPs in layered oxides such as V_2O_5,[37,244–267] or MoO_3,[268–273] layered transition metal sulfides such as MoS_2,[274–276] chlorides such as $RuCl_3$,[277] and oxychlorides such as $FeOCl$,[35,278–284] silicates and phosphates[285] (α-$VOPO_4$,[286] UO_2PO_4,[287] $CdPS_3$, and $NiPS_3$[272]) as well as the insertion within the channels of zeolitic solids.[285,288–294] A related large group of hybrids formed by COPs and inorganic polymers of the Prussian blue family ($Fe[Fe(CN)_6]$)[295–301] can also be considered within this category, although in that case the structure of the hybrid and its intercalate nature are less well established.

One of the most extensively studied and better characterized IO systems is the family of hybrids based on V_2O_5 as the inorganic host. We can analyze it in more detail as a representative example of IO hybrid materials. Indeed, there have been a few major lines of work dealing with several hybrids: PAni–V_2O_5,[244–260] PPy–V_2O_5,[37,245–248,254,261–265,267] and PT–V_2O_5.[245,246,266,267] For a given hybrid, the inorganic starting matrix could be either crystalline V_2O_5 or the quasi-amorphous V_2O_5 xerogel material obtained by drying the gel resulting from the acidic hydrolysis of vanadate.[302,303] Most studies have been based on the latter, aiming at the production of hybrids interacting at the molecular level with reduced kinetic barriers for their formation, although hybrids based on crystalline V_2O_5 have also been reported.[256]

As for any other IO intercalation material, the formation of hybrids of COPs inserted in V_2O_5 takes place with the initial intercalation of the corresponding monomer molecules into the inorganic layered structure. The strongly oxidizing character of the oxide induces the redox polymerization of the organic molecules. It is worth remarking that while the inserted polymer is effectively p-doped (partially oxidized) during this process, the V_2O_5 oxide suffers itself a partial reduction that renders it an n-doped (partially reduced) electrically conductive mixed-valence (V^{IV}/V^V) oxide.[244,253] Thus, in this process, a mutual doping takes place during redox intercalative polymerization, leading to a material with a double conduction mechanism.

Earlier work on COPs-inserted V_2O_5 centered on the study of the intercalative oxidation process itself and relied upon the use of preformed films of V_2O_5 xerogel for the intercala-

tion of the monomers. Vanadium pentoxide gels can indeed easily form highly oriented films that yield characteristic powder X-ray diffraction patterns with enhanced 00*l* peaks (Fig. 4a). On the other hand, a powder sample of a V_2O_5 xerogel will show a diffraction pattern with more peaks but with an apparently poorer crystallinity (Fig. 4b). The process of
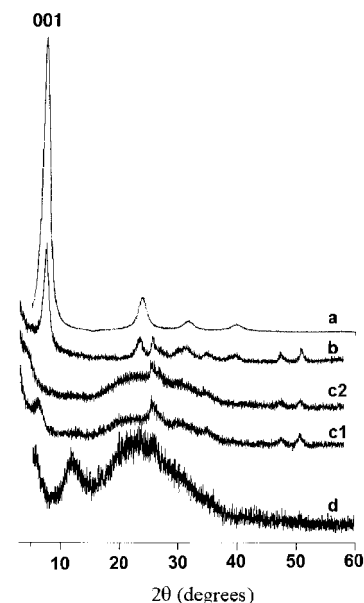

Fig. 4. X-ray diffraction patterns for V_2O_5 and related hybrid materials. a) Oriented films of V_2O_5 showing preferential orientation (enhanced intensity for 00*l* peaks). b) V_2O_5 xerogel powder. c1) PAni–V_2O_5 hybrid with a monolayer of PAni inserted in the oxide (001 peak indicates a spacing of 14 Å). c2) PAni–V_2O_5 hybrid with a double layer of PAni inserted in the oxide (001 peak indicates a spacing of 22 Å). d) PAni–V_2O_5 hybrid prepared for an extended period of 194 h (as compared with 1 h for samples c1 and c2).

formation of PAni-inserted V_2O_5 films has been studied in detail[244–247,249,253] and presents certain characteristics which indicate its complex nature. Thus, the initial intercalation of aniline monomers into the inorganic phase takes place with a concomitant polymerization process.

However, after this first stage follows a process of aging with further oxidative polymerization driven by molecular oxygen, resulting in the extension of the PAni chains and with V_2O_5 undergoing an overall oxidation itself and acting as a catalyst of the polymerization process.[253] The final result is a hybrid material where the inserted PAni is in its conductive poly-emeraldine salt form and occupies the constrained interlayer spaces of V_2O_5.

From a crystal-chemical point of view the PAni–V_2O_5 hybrid formation is associated with an expansion of the interlayer spacing characteristic of V_2O_5. In the gels and xerogels that space is occupied by variable amounts of water molecules which in the xerogel lead to a characteristic value for the *c*-axis of 11.55 Å. In the PAni–V_2O_5 hybrid the shift of the prominent 001 peak in the X-ray diffraction pattern (Fig. 4c1) indicates a *c*-axis of ca. 14 Å (13.94 Å[244]) which is consistent with the substitution of the water molecules by PAni.

Furthermore, a systematic study of aniline-rich reaction mixtures has shown that it is possible to identify two interca-

late phases among polycrystalline PAni–V_2O_5 hybrids, corresponding to a single and a double layer of PAni inserted in the inter-layer space.[260] Traces c1 and c2 in Figure 4 correspond to these single and double intercalates which show spacings of ca. 14 Å and 22 Å respectively. Figure 5 shows schematic drawings and spacings corresponding to these materials and the hydrated xerogel.
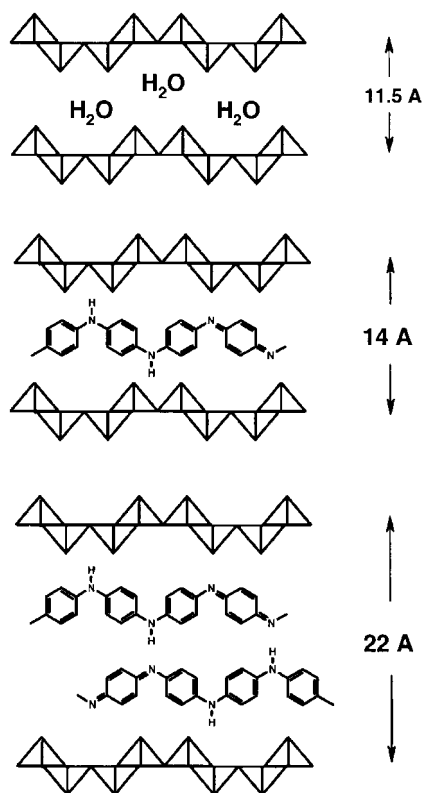

Fig. 5. Schematic representation of the structures of the hydrated V_2O_5 xerogel as well as the single- and double-layer intercalates of PAni/V_2O_5 hybrids. The spacings indicated were calculated from the angular position of peaks 001 in each case (see Fig. 4).

In addition to the intercalative polymerization of aniline into preformed V_2O_5 films, an alternative synthetic method has also been used for the synthesis of PAni–V_2O_5 hybrid materials.[255,257–260] The "in-situ" formation of the hybrid relies upon polymerization of aniline monomers added directly to the freshly formed V_2O_5 hydrogel, followed by isolation and drying of the hybrid formed.[260] This approach leads to very poorly crystalline compounds, almost amorphous materials as evidenced by the very broad diffraction peaks (traces in Fig. 4c correspond to these samples). In these materials the structural integrity of V_2O_5 layered ribbons is only marginally retained. Indeed, for longer reaction times, aged materials shift from truly IO hybrids with a V_2O_5 dominated structure to materials in which the structure of the organic chains seems to take over.[255] This is evidenced by the final loss of crystallinity in Figure 4d, an X-ray diffraction pattern where peaks characteristic of V_2O_5 have disappeared and only diffuse scattering features from the polymer remain. This can therefore be considered a bor-

derline case between IO and OI hybrids and could be rightfully labeled as a hybrid polymeric material.

Recent interest in PAni–V_2O_5 hybrids has centered on their electrochemical properties and possible application as insertion cathodes in reversible lithium cells.[248,250,252,254–259] Figure 6 shows initial charge–discharge cycles of lithium batteries set up with different hybrid materials and the related V_2O_5
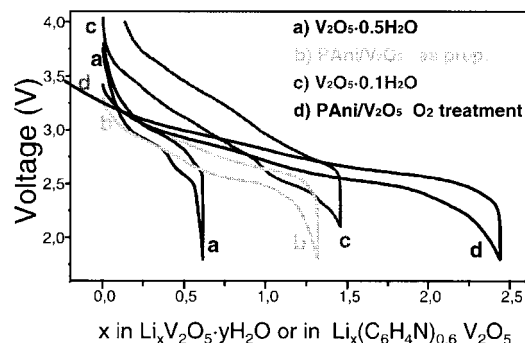

Fig. 6. Initial cycles of discharge and charge for reversible lithium cells using the compounds indicated as active cathode materials in front of lithium anodes (from [257]).

xerogels. The electrochemical performance of these materials is very sensitive to the nature of the polymer and the composition of the hybrid; thus, the synthesis conditions and subsequent treatments are of the greatest importance. For example, O_2 treatment which, as discussed above, has an important effect on the final molecular weight of the polymer and on the oxidation state of the oxide, is of great help in controlling the specific capacity of these hybrid cathodes,[254,257] which can reach values as high as 300 A h/kg[257] (Fig. 6d).

It should be noted that the hybrid materials benefit from the electrochemical activity of both organic and inorganic components and that both contributions effectively correspond to the intercalation of cations, making the material useful within the optimal source–sink reversible cell mechanism. However, in addition, there are features like the improved diffusion of lithium[254] (Li$^+$ diffusion coefficients were found to be one order of magnitude higher in the hybrids than in the parent V_2O_5 xerogel) or the increased capacity of the PAni–V_2O_5 combination[257] that make the performance of the hybrid superior to the sum of its components, in a characteristic synergic behavior.[254,257]

6. Conclusions, Prospects, and Applications

The design of hybrid materials based on COPs has thrived during the last decade. After an initial period of rediscovery of conjugated polymers as conducting materials in the seventies and after a period of detailed studies of their properties and possible applications, came the realization that COPs could also be used as components of more complex systems and, in particular, part of hybrid materials which could merge the best properties of both the organic polymers and inorganic species. This broad goal has been tackled using many different

ADVANCED MATERIALS

approaches, leading to a wide variety of materials. Examples range from organic polymer structures doped with inorganic molecular species (OI materials) to hybrids of the inverse nature where extended inorganic host structures incorporate the conducting polymers (IO materials). In between are materials where no structure clearly dominates or where nanosized particles are dispersed in the polymers forming nanocomposite materials.

Hybrid materials have been prepared as bulk powders or as electrochemically grown films. The polymers used have been primarily PPy (119) and PAni (84) although PT and its derivatives (25), PAc (11), poly(*p*-phenylenevinylene) (7), and, to a lesser extent, other conducting polymers have also been used (numbers in parentheses indicate the corresponding number of references in the present work). However, common to all these hybrid materials is the underlying search for synergy. Whether we just seek a material with the mechanical properties of the polymer as a support or a hybrid where the activities of the organic and inorganic species reinforce each other, the hybrid approach tries in general to create materials that are superior to the sum of their parts. This synergy is implicit in most of the work referenced here but has also been explicitly discussed in the case of PAni–V_2O_5 hybrid electrodes and related insertion phases[254,257,258,285] or in the activity of nanocomposites of polypyrrole and carbon black towards reduction of Cr^{VI}.[215]

The fields of application of this branch of materials are as varied as the materials themselves. A large number of the hybrids described here are based on electro-active inorganic compounds and of course COPs themselves are electro-active. This prompted the development of applications like electrocatalysis[72,304] or energy storage[182] where the electrochemical activity is paramount. Electro-catalytic reactions studied with hybrid electrodes range from the reduction of O_2[127,207] and protons[142,208] or the oxidation of H_2,[49] oxidation[74,137] or hydrogenation[82] of organic substrates or inorganic oxoanions,[176] electrocatalytic reduction of CO_2,[300] or environmental pollution abatement by electro-reduction of Cr^{VI}.[215] On the other hand, concerning energy-storage applications, materials for supercapacitors[211] as well as for insertion electrodes in rechargeable lithium batteries[221,257,267] have been developed. Examples of other applications include the harnessing of electrochromic,[86,139,230,232] and photoelectrochromic[241] properties, application in display devices,[241] photovoltaics,[229] and novel energy-conversion systems,[227] proton-pump electrodes,[203] sensors,[32] or chemiresistive detectors, which work as artificial "noses" and already outperform human olfaction in detecting, for example, biogenic amines.[216]

The applications of hybrid materials are promising and varied but in addition to improved devices, hybrid compounds are also interesting from a fundamental point of view. Thus, the anchoring of isolated ions or molecules within an electron-conducting polymeric matrix offers the opportunity to study the chemistry and electrochemistry of those compounds in isolation, thus blocking the possibility of isomolecular interactions leading normally to clustering or precipitation processes. This approach, which we could call matrix chemistry[255] could for instance allow the study of the redox chemistry of manganese or iron species without the predictable condensation to form MnO_2 or μ-oxo Fe^{III} dimers, respectively, which frequently takes place in solution chemistry.

Also from a fundamental point of view, much remains to be learned about the structural features of hybrid materials in general. For instance, in IO hybrids the field is quite open to modeling and study of the conformation of the polymers upon insertion into the inorganic matrix, whereas in OI hybrids the effect of charge and size of doping species on polymeric conformation is even less well known.

As a final remark, we can conclude that the vigorous development of this field that has taken place during just the last decade allows us to expect new exciting developments dealing with both fundamental aspects and applications of functional hybrid materials.

[1] The word adobe is of Spanish-Moorish origin, but adobe constructions are found from the east Mediterranean, North Africa, and southern Spain to many pre- and post-Columbian sites from the United States to Peru, always in regions with a dry climate.

[2] H. R. Allcock, *Adv. Mater.* **1994**, *6*, 106.

[3] B. M. Novak, *Adv. Mater.* **1993**, *5*, 422.

[4] D. A. Loy, K. J. Shea, *Chem. Rev.* **1995**, *95*, 1431.

[5] P. Judeinstein, C. Sanchez, *J. Mater. Chem.* **1996**, *6*, 511.

[6] K. G. Sharp, *Adv. Mater.* **1998**, *10*, 1243.

[7] C. Sanchez, F. Ribot, B. Lebeau, *J. Mater. Chem.* **1999**, *9*, 35.

[8] P. Judeinstein, H. Schmidt, *J. Sol–Gel Sci. Technol.* **1994**, *3*, 189.

[9] J. H. Harreld, B. Dunn, J. I. Zink, *J. Mater. Chem.* **1997**, *7*, 1511.

[10] C. Roscher, R. Buestrich, P. Dannberg, O. Rosch, M. Popall, *Mater. Res. Soc. Symp. Proc.* **1998**, *519*, 239.

[11] H. K. Kim, S.-J. Kang, S.-K. Choi, Y.-H. Min, C.-S. Yoon, *Chem. Mater.* **1999**, *11*, 779.

[12] J. Livage, C. Sanchez, *Mol. Cryst. Liq. Cryst. S&T Sect. B: Nonlinear Opt.* **1999**, *21*, 125.

[13] S. P. Armes, S. Maeda, M. Gill, *Polym. Mater. Sci. Eng.* **1993**, *70*, 352.

[14] M. Mager, F. Jonas, A. Eiling, U. Guntermann, *German Patent 19650147 A1*, **1998**.

[15] S. Dire, F. Babonneau, C. Sanchez, J. Livage, *J. Mater. Chem.* **1992**, *2*, 239.

[16] N. I. Koslova, B. Viana, C. Sanchez, *J. Mater. Chem.* **1993**, *3*, 111.

[17] S. M. Jones, S. E. Friberg, *J. Mater. Sci.* **1996**, *31*, 1475.

[18] E. Cordoncillo, B. Viana, P. Escribano, C. Sanchez, *J. Mater. Chem.* **1998**, *8*, 507.

[19] V. de Zea Bermudez, L. D. Carlos, M. C. Duarte, M. M. Silva, C. J. R. Silva, M. J. Smith, M. Assuncao, L. Alcacer, *J. Alloys Compd.* **1998**, *275–277*, 21.

[20] T. Dantas de Morais, F. Chaput, K. Lahlil, J.-P. Boilot, *Adv. Mater.* **1999**, *11*, 107.

[21] T. Fujinami, K. Sugie, K. Mori, M. A. Mehta, *Chem. Lett.* **1998**, *7*, 619.

[22] L. Depre, J. Kappel, M. Popall, *Electrochim. Acta* **1998**, *43*, 1301.

[23] I. Honma, Y. Takeda, J. M. Bae, *Solid State Ionics* **1999**, *120*, 255.

[24] P. Hernan, C. Del Pino, E. Ruiz-Hitzky, *Chem. Mater.* **1992**, *4*, 49.

[25] P. Aranda, A. Jimenez-Morales, J. C. Galvan, B. Casal, E. Ruiz-Hitzky, *J. Mater. Chem.* **1995**, *5*, 817.

[26] M. Barboiu, C. Luca, C. Guizard, N. Hovnanian, L. Cot, G. Popescu, *J. Membr. Sci.* **1997**, *129*, 197.

[27] A. Jimenez-Morales, J. C. Galvan, P. Aranda, E. Ruiz-Hitzky, *Mater. Res. Soc. Symp. Proc.* **1998**, *519*, 211.

[28] P. Battioni, E. Cardin, M. Louloudi, B. Schollhorn, G. A. Spyroulias, D. Mansuy, T. G. Traylor, *Chem. Commun.* **1996**, *17*, 2037.

[29] M. Buechler-Skoda, R. Gill, D. Vu, C. Nguyen, G. Larsen, *Appl. Catal. A* **1999**, *2*, 185.

[30] K. J. Ciuffi, H. C. Sacco, J. B. Valim, C. M. C. P. Manso, O. A. Serra, O. R. Nascimento, E. A. Vidoto, Y. Iamamoto, *J. Non-Cryst. Solids* **1999**, *247*, 146.

[31] M. T. Reetz, *Adv. Mater.* **1997**, *9*, 943.

[32] B. Wang, B. Li, Q. Deng, S. Dong, *Anal. Chem.* **1998**, *70*, 3170.

[33] J. D. Brennan, J. S. Hartman, E. I. Ilnicki, M. Rakic, *Chem. Mater.* **1999**, *11*, 1853.

[34] E. Ruiz-Hitzky, B. Casal, *Nature* **1978**, *276*, 596.

[35] M. G. Kanatzidis, L. M. Tonge, T. J. Marks, H. O. Marcy, C. R. Kannewurf, *J. Am. Chem. Soc.* **1987**, *109*, 3797.

[36] B. Casal, E. Ruiz-Hitzky, M. Crespin, D. Tinet, J. C. Galvan, *J. Chem. Soc., Faraday Trans. 1* **1989**, *12*, 85.

[37] C. G. Wu, M. G. Kanatzidis, H. O. Marcy, D. C. DeGroot, C. R. Kannewurf, *Polym. Mater. Sci. Eng.* **1989**, *61*, 969.

[38] K. Chibwe, W. Jones, *J. Chem. Soc., Chem. Commun.* **1989**, 14.

[39] J. W. Johnson, A. J. Jacobson, W. M. Butler, S. E. Rosenthal, J. F. Brody, J. T. Lewandowski, *J. Am. Chem. Soc.* **1989**, *111*, 381.

[40] B. Ackermans, R. A. Schoonheydt, E. Ruiz-Hitzky, *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 4479.

[41] P. Gomez-Romero, M. Lira-Cantu, *Adv. Mater.* **1997**, *9*, 144.

[42] D. E. Fogg, L. H. Radzilowski, B. O. Dabbousi, R. R. Schrock, E. L. Thomas, M. G. Bawendi, *Macromolecules* **1997**, *30*, 8433.

[43] F. Ribot, C. Sanchez, *Comments Inorg. Chem.* **1999**, *20*, 327.

[44] C. H. Lee, G. Yu, D. Moses, K. Pakbaz, C. Zhang, N. S. Sariciftci, A. J. Heeger, F. Wudl, *Phys. Rev. B: Condens. Matter* **1993**, *48*, 15 425.

[45] G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, *Science* **1995**, *270*, 1789.

[46] A. Deronzier, J.-C. Moutet, P. Seta, *J. Am. Chem. Soc.* **1994**, *116*, 5019.

[47] S. Bouchtalla, A. Deronzier, J. M. Janot, J. C. Moutet, P. Seta, *Synth. Met.* **1996**, *82*, 129.

[48] K. Yoshino, Y. Kawagishi, S. Tatsuhara, H. Kajii, S. Lee, M. Ozaki, Z. V. Vardeny, A. A. Zakhidov, *Superlattices Microstruct.* **1999**, *25*, 325.

[49] C. C. Chen, C. S. C. Bose, K. Rajeshwar, *J. Electroanal. Chem.* **1993**, *350*, 161.

[50] M. Hasik, A. Drelinkiewicz, M. Choczynski, S. Quillard, A. Pron, *Synth. Met.* **1997**, *84*, 93.

[51] H.-S. Li, M. Josowicz, D. R. Baer, M. H. Engelhard, J. Janata, *J. Electrochem. Soc.* **1995**, *142*, 798.

[52] J. Livage, *Bull. Mater. Sci.* **1999**, *22*, 201.

[53] P. Behrens, *Organosilicon Chem. III*, 3rd Muench. Silicontage **1998**.

[54] P. Aranda, J. C. Galvan, B. Casal, E. Ruiz-Hitzky, *Electrochim. Acta* **1992**, *37*, 1573.

[55] B. Casal, P. Aranda, J. Sanz, E. Ruiz-Hitzky, *Clay Miner.* **1994**, *29*, 191.

[56] P. Aranda, B. Casal, J. J. Fripiat, E. Ruiz-Hitzky, *Langmuir* **1994**, *10*, 1207.

[57] E. Ruiz-Hitzky, P. Aranda, *Adv. Mater.* **1990**, *2*, 545.

[58] P. Aranda, E. Ruiz-Hitzky, *Chem. Mater.* **1992**, *4*, 1395.

[59] P. Aranda, E. Ruiz-Hitzky, *Acta Polym.* **1994**, *45*, 59.

[60] P. Aranda, J. C. Galvan, E. Ruiz-Hitzky, *Mater. Res. Soc. Symp. Proc.* **1998**, *519*, 375.

[61] Z. Shen, G. P. Simon, Y. B. Cheng, *J. Australas. Ceram. Soc.* **1998**, *34*, 1.

[62] P. Aranda, E. Ruiz-Hitzky, *Appl. Clay Sci.* **1999**, *15*, 119.

[63] J. S. Miller, *Adv. Mater.* **1993**, *5*, 587.

[64] J. S. Miller, *Adv. Mater.* **1993**, *5*, 671.

[65] G. P. Evans, in *Advances in Electrochemical Science and Engineering*, Vol. 1 (Eds: H. Gerischer, C. W. Tobias), VCH, Weinheim **1990**, p. 1.

[66] P. Baeuerle, *Adv. Mater.* **1993**, *5*, 879.

[67] A. O. Patil, A. J. Heeger, F. Wudl, *Chem. Rev.* **1988**, *88*, 183.

[68] S. Roth, M. Filzmoser, *Adv. Mater.* **1990**, *2*, 356.

[69] M. J. Sailor, C. L. Curtis, *Adv. Mater.* **1994**, *6*, 688.

[70] P. Novak, K. Mueller, K. S. V. Santhanam, O. Haas, *Chem. Rev.* **1997**, *97*, 207.

[71] R. D. McCullough, *Adv. Mater.* **1998**, *10*, 93.

[72] A. Deronzier, J.-C. Moutet, *Coord. Chem. Rev.* **1996**, *147*, 339.

[73] A. Deronzier, J. M. Latour, *J. Electroanal. Chem. Interfacial Electrochem.* **1987**, *224*, 295.

[74] P. Moisy, F. Bedioui, Y. Robin, J. Devynck, *J. Electroanal. Chem. Interfacial Electrochem.* **1988**, *250*, 191.

[75] P. Moisy, F. Bedioui, J. Devynck, L. Salmon, C. Bied-Charreton, *New J. Chem.* **1989**, *13*, 511.

[76] F. Bedioui, P. Moisy, J. Devynck, L. Salmon, C. Bied-Charreton, *J. Mol. Catal.* **1989**, *56*, 267.

[77] C. Armengaud, P. Moisy, F. Bedioui, J. Devynck, C. Bied-Charreton, *J. Electroanal. Chem. Interfacial Electrochem.* **1990**, *277*, 197.

[78] F. Bedioui, M. Voisin, J. Devynck, C. Bied-Charreton, *J. Electroanal. Chem. Interfacial Electrochem.* **1991**, *297*, 257.

[79] A. Deronzier, R. Devaux, D. Limosin, J. M. Latour, *J. Electroanal. Chem.* **1992**, *324*, 325.

[80] W. F. De Giovani, A. Deronzier, *J. Chem. Soc., Chem. Commun.* **1992**, 19.

[81] M. A. Carvalho de Medeiros, S. Cosnier, A. Deronzier, J.-C. Moutet, *Inorg. Chem.* **1996**, *35*, 2659.

[82] A. Deronzier, J.-C. Moutet, *Platinum Met. Rev.* **1998**, *42*, 60.

[83] A. Deronzier, P. Jardon, A. Martre, J.-C. Moutet, C. Santato, V. Balzani, A. Credi, F. Paolucci, S. Roffia, *New J. Chem.* **1998**, *22*, 33.

[84] A. Deronzier, D. Eloy, P. Jardon, A. Martre, J.-C. Moutet, *J. Electroanal. Chem.* **1998**, *453*, 179.

[85] G. King, S. J. Higgins, N. Price, *Analyst (London)* **1992**, *117*, 1243.

[86] J. L. Reddinger, J. R. Reynolds, *Macromolecules* **1997**, *30*, 673.

[87] K. A. Macor, Y. O. Su, L. A. Miller, T. G. Spiro, *Inorg. Chem.* **1987**, *26*, 2594.

[88] J. Przyluski, M. Zagorska, A. Pron, Z. Kucharski, J. Suwalski, *J. Phys. Chem. Solids* **1987**, *48*, 635.

[89] A. Pron, J. Suwalski, S. Lefrant, *Synth. Met.* **1987**, *18*, 25.

[90] S. Flandrois, A. Boukhari, A. Pron, M. Zagorska, *Solid State Commun.* **1988**, *67*, 471.

[91] I. Kulszewicz-Bajer, A. Pawlicka, J. Plenkiewicz, A. Pron, S. Lefrant, *Synth. Met.* **1989**, *30*, 335.

[92] J. F. Rabek, J. Lucki, M. Zuber, B. J. Qu, W. F. Shi, *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1990**, *2*, 31.

[93] M. S. A. Abdou, S. Holdcroft, *Chem. Mater.* **1994**, *6*, 962.

[94] M. Zagorska, H. Wycislik, J. Przyluski, *Synth. Met.* **1987**, *20*, 259.

[95] L. L. Miller, B. Zinger, Q. X. Zhou, *J. Am. Chem. Soc.* **1987**, *109*, 2267.

[96] J. Tietje-Girault, J. M. Anderson, I. MacInnes, M. Schroder, G. Tennant, H. H. Girault, *J. Chem. Soc., Chem. Commun.* **1987**, 14.

[97] G. Lian, S. Dong, *J. Electroanal. Chem. Interfacial Electrochem.* **1989**, *260*, 127.

[98] H. Mao, P. G. Pickup, *J. Phys. Chem.* **1989**, *93*, 6480.

[99] S. Dong, G. Lian, *J. Electroanal. Chem. Interfacial Electrochem.* **1990**, *291*, 23.

[100] W. Breen, J. F. Cassidy, M. E. G. Lyons, *J. Electroanal. Chem. Interfacial Electrochem.* **1991**, *297*, 445.

[101] J. Han, S. Lee, W. K. Paik, *Bull. Korean Chem. Soc.* **1992**, *13*, 419.

[102] S. Lee, J. Han, W. K. Paik, *Synth. Met.* **1993**, *55*, 1129.

[103] A. P. Chattaraj, I. N. Basumallick, *J. Power Sources* **1993**, *45*, 237.

[104] M. Tolgyesi, A. Szucs, C. Visy, M. Novak, *Electrochim. Acta* **1995**, *40*, 1127.

[105] H. Sung, T. Lee, W.-K. Paik, *Synth. Met.* **1995**, *69*, 485.

[106] G. Torres-Gomez, P. Gomez-Romero, *Synth. Met.* **1998**, *98*, 95.

[107] G. Torres-Gomez, M. Lira-Cantu, P. Gomez-Romero, *J. New Mater. Electrochem. Syst.* **1999**, *2*, 145.

[108] G. Torres-Gomez, K. West, S. Skaarup, P. Gomez-Romero, *J. Electrochem. Soc.* **2000**, *147*, 2513.

[109] P. Gomez-Romero, G. Torres-Gomez, *Adv. Mater.* **2000**, *12*, 1454.

[110] R. Cervini, R. J. Fleming, K. S. Murray, *J. Mater. Chem.* **1992**, *2*, 1115.

[111] R. Cervini, R. J. Fleming, B. J. Kennedy, K. S. Murray, *J. Mater. Chem.* **1994**, *4*, 87.

[112] M. Takakubo, *Synth. Met.* **1987**, *18*, 53.

[113] N. S. Allen, K. S. Murray, R. J. Fleming, B. R. Saunders, *Synth. Met.* **1997**, *87*, 237.

[114] B. R. Saunders, K. S. Murray, R. J. Fleming, D. G. McCulloch, L. J. Brown, J. D. Cashion, *Chem. Mater.* **1994**, *6*, 697.

[115] B. R. Saunders, R. J. Fleming, K. S. Murray, *Chem. Mater.* **1995**, *7*, 1082.

[116] D. Belanger, G. Laperriere, L. Gravel, *J. Electrochem. Soc.* **1990**, *137*, 365.

[117] F. Girard, S. Ye, G. Laperriere, D. Belanger, *J. Electroanal. Chem.* **1992**, *334*, 35.

[118] S. Ye, F. Girard, D. Belanger, *J. Phys. Chem.* **1993**, *97*, 12 373.

[119] D. Belanger, G. Laperriere, F. Girard, D. Guay, G. Tourillon, *Chem. Mater.* **1993**, *5*, 861.

[120] F. Girard, S. Ye, D. Belanger, *J. Electrochem. Soc.* **1995**, *142*, 2296.

[121] S. Lavallee, G. Laperriere, D. Belanger, *J. Electroanal. Chem.* **1997**, *431*, 219.

[122] F. Fusalba, D. Belanger, *J. Mater. Res.* **1999**, *14*, 1805.

[123] B. Garcia, F. Roy, D. Belanger, *J. Electrochem. Soc.* **1999**, *146*, 226.

[124] R. A. Bull, F.-R. Fan, A. J. Bard, *J. Electrochem. Soc.* **1983**, *130*, 1636.

[125] S. Kuwabata, K. Okamoto, O. Ikeda, H. Yoneyama, *Synth. Met.* **1987**, *18*, 101.

[126] A. Elzing, A. Van der Putten, W. Visscher, E. Barendrecht, *J. Electroanal. Chem. Interfacial Electrochem.* **1987**, *233*, 113.

[127] R. Jiang, S. Dong, *J. Electroanal. Chem. Interfacial Electrochem.* **1988**, *246*, 101.

[128] C. S. Choi, H. Tachikawa, *J. Am. Chem. Soc.* **1990**, *112*, 1757.

[129] M. Kawashima, H. Tanaka, M. Sakaguchi, *J. Electroanal. Chem. Interfacial Electrochem.* **1990**, *286*, 123.

[130] M. Zagorska, I. Kulszewicz-Bajer, E. Lukomska-Godzisz, A. Pron, I. Glowacki, J. Ulanski, S. Lefrant, *Synth. Met.* **1990**, *37*, 99.

[131] I. Kulszewicz-Bajer, M. Zagorska, A. Pron, D. Billaud, J. J. Ehrhardt, *Mater. Res. Bull.* **1991**, *26*, 163.

[132] I. Kulszewicz-Bajer, M. Zagorska, J. Pozniczek, A. Bielanski, K. Kruczala, K. Dyrek, A. Pron, *Synth. Met.* **1991**, *41*, 39.

[133] J. Pozniczek, I. Kulszewicz-Bajer, M. Zagorska, K. Kruczala, K. Dyrek, A. Bielanski, A. Pron, *J. Catal.* **1991**, *132*, 311.

[134] B. R. Saunders, K. S. Murray, R. J. Fleming, *Synth. Met.* **1992**, *47*, 167.

[135] B. R. Saunders, K. S. Murray, R. J. Fleming, Y. Korbatieh, *Chem. Mater.* **1993**, *5*, 809.

[136] B. R. Saunders, K. S. Murray, R. J. Fleming, D. G. McColloch, *Synth. Met.* **1995**, *69*, 363.

[137] I. De Gregori, M. Carrier, A. Deronzier, J. C. Moutet, F. Bedioui, J. Devynck, *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 1567.

[138] F. Bedioui, Y. Bouchier, C. Sorel, J. Devynck, L. Coche-Guerrente, A. Deronzier, J. C. Moutet, *Electrochim. Acta* **1993**, *38*, 2485.

[139] T. Shimidzu, A. Ohtani, M. Aiba, K. Honda, *J. Chem. Soc., Faraday Trans.* **1988**, *84*, 3941.

[140] M. Zaragoza, A. Pron, *Synth. Met.* **1987**, *18*, 123.

[141] G. Bidan, E. M. Genies, M. Lapkowski, *J. Electroanal. Chem. Interfacial Electrochem.* **1988**, *251*, 297.

[142] G. Bidan, E. M. Genies, M. Lapkowski, *J. Chem. Soc., Chem. Commun.* **1988**, *5*, 533.

[143] B. Keita, D. Bouaziz, L. Nadjo, *J. Electroanal. Chem. Interfacial Electrochem* **1988**, *255*, 303.

[144] B. Keita, L. Nadjo, *J. Electroanal. Chem.* **1988**, *240*, 325.

[145] B. Keita, L. Nadjo, J. P. Haeussler, *J. Electroanal. Chem.* **1988**, *243*, 481.

[146] G. Bidan, E. Genies, M. Laprowski, *Eur. Patent Appl. EP 323 351*, **1989**.

[147] G. Bidan, E. M. Genies, M. Lapkowski, *Synth. Met.* **1989**, *31*, 327.

[148] G. Bidan, M. Lapkowski, J. P. Travers, *Synth. Met.* **1989**, *28*, C113.

[149] B. Keita, D. Bouaziz, L. Nadjo, A. Deronzier, *J. Electroanal. Chem. Interfacial Electrochem* **1990**, *279*, 187.

[150] S. Dong, B. Wang, F. Song, *Chin. Chem. Lett.* **1991**, *2*, 411.

[151] M. Lapkowski, G. Bidan, M. Fournier, *Synth. Met.* **1991**, *41*, 407.

[152] M. Lapkowski, G. Bidan, M. Fournier, *Synth. Met.* **1991**, *41*, 411.

[153] M. Lapkowski, G. Bidan, M. Fournier, *Pol. J. Chem.* **1991**, *65*, 1547.

[154] J. Pozniczek, A. Bielanski, I. Kulszewiez-Bajer, M. Zargorska, A. Pron, *J. Mol. Catal.* **1991**, *69*, 223.

[155] A. Pron, *Synth. Met.* **1992**, *46*, 277.

[156] W. Baoxing, S. Fayi, D. Shaojun, *J. Electroanal. Chem.* **1993**, *353*, 43.

[157] S. Dong, W. Jin, *J. Electroanal. Chem.* **1993**, *3*, 87.

[158] B. Fabre, G. Bidan, *Adv. Mater.* **1993**, *5*, 646.

[159] M. Hasik, A. Pron, I. Kulszewiczbajer, J. Pozniczek, A. Bielanski, Z. Piwowarska, R. Dziembaj, *Synth. Met.* **1993**, *55*, 972.

[160] B. X. Wang, F. Y. Song, S. J. Dong, *J. Electroanal. Chem.* **1993**, *353*, 43.

[161] S. Dong, M. Liu, *Electrochim. Acta* **1994**, *39*, 947.

[162] M. Hasik, J. Pozniczek, Z. Piwowarska, R. Dziembaj, A. Bielanski, A. Pron, *J. Mol. Catal.* **1994**, *89*, 329.

[163] M. Hasik, A. Pron, J. Pozniczek, A. Bielanski, Z. Piwowarska, K. Kruczala, R. Dziembaj, *J. Chem. Soc. Faraday Trans.* **1994**, *90*, 2099.

[164] M. Hasik, W. Turek, E. Stochmal, M. Lapkowski, A. Pron, *J. Catal.* **1994**, *147*, 544.

[165] V. W. Jones, M. Kalaji, G. Walker, C. Barbero, R. Kotz, *J. Chem. Soc. Faraday Trans.* **1994**, *90*, 2061.

[166] H. Sung, H. So, W. K. Paik, *Electrochim. Acta* **1994**, *39*, 645.

[167] K. Cho, S. D. Chung, J. Ryu, Y. Kim, J. Choy, H. Kim, *Synth. Met.* **1995**, *69*, 481.

[168] M. Freund, C. Karp, N. S. Lewis, *Inorg. Chim. Acta* **1995**, *240*, 447.

[169] B. Keita, A. Mahmoud, L. Nadjo, *J. Electroanal. Chem.* **1995**, *386*, 245.

[170] I. Kulszewicz-Bajer, I. Wielgus, J. W. Sobczak, K. Kruczala, A. Pron, *Mater. Res. Bull.* **1995**, *30*, 1571.

[171] M. Lapkowski, W. Turek, M. Barth, S. Lefrant, *Synth. Met.* **1995**, *69*, 127.

[172] M. Liu, S. Dong, *Electrochim. Acta* **1995**, *40*, 197.

[173] M. Barth, W. Turek, M. Lapkowski, *Pol. J. Appl. Chem.* **1996**, *39(2)*, 271.

[174] P. Gomez-Romero, N. Casan-Pastor, *J. Phys. Chem.* **1996**, *100*, 12 448.

[175] P. Wang, Y. F. Li, *J. Electroanal. Chem.* **1996**, *408*, 77.

[176] B. Fabre, G. Bidan, *Electrochim. Acta* **1997**, *42*, 2587.

[177] B. Fabre, G. Bidan, *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 591.

[178] P. Gomez-Romero, *Solid State Ionics* **1997**, *101–103*, 243.

[179] P. Gomez-Romero, N. Casan-Pastor, M. Lira-Cantu, *Solid State Ionics* **1997**, *101–103*, 875.

[180] P. Gomez-Romero, M. Lira-Cantu, *Proc. Electrochem. Soc.* **1997**, *96–17*, 158.

[181] M. Lira-Cantu, *Chemistry*, Universitat Autonoma de Barcelona **1997**, p. 244.

[182] M. Lira-Cantu, P. Gomez-Romero, *Recent Res. Dev. Phys. Chem.* **1997**, *1*, 379.

[183] M. Lira-Cantu, P. Gomez-Romero, *Ionics* **1997**, *3*, 194.

[184] P. Gomez-Romero, M. Lira-Cantu, N. Casan-Pastor, *Spanish Patent ES 2 120 324 A1 16*, **1998**.

[185] M. Lira-Cantu, P. Gomez-Romero, *Chem. Mater.* **1998**, *10*, 698.

[186] A. Mahmoud, B. Keita, L. Nadjo, *J. Electroanal. Chem.* **1998**, *446*, 211.

[187] M. Barth, M. Lapkowski, S. Lefrant, *Electrochim. Acta* **1999**, *44*, 2117.

[188] A. Mahmoud, B. Keita, L. Nadjo, O. Oung, R. Contant, S. Brown, Y. de Kouchkovsky, *J. Electroanal. Chem.* **1999**, *463*, 129.

[189] M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, Berlin **1983**.

[190] M. T. Pope, A. Müller, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 34.

[191] M. T. Pope, A. Müller, in *Topics in Molecular Organization and Engineering*, Vol. 10, Kluwer, Dordrecht, The Netherlands **1994**.

[192] A. Muller, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2122.

[193] B. Tell, *J. Electrochem. Soc.* **1980**, *127*, 2451.

[194] E. Papaconstantinou, *Chem. Soc. Rev.* **1989**, *18*, 1.

[195] N. Casañ-Pastor, L. C. W. Baker, *J. Am. Chem. Soc.* **1992**, *114*, 10 384.

[196] N. Casañ-Pastor, J. Bas-Serra, E. Coronado, L. C. Baker, *J. Am. Chem. Soc.* **1992**, *114*, 10 380.

[197] R. F. Renneke, C. L. Hill, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1526.

[198] S. F. Jen, A. B. Anderson, C. L. Hill, *J. Phys. Chem.* **1992**, *96*, 5658.

[199] J. Y. Lim, W.-K. Paik, I.-H. Yeo, *Synth. Met.* **1995**, *69*, 451.

[200] N. Furukawa, K. Nishio, in *Applications of Electroactive Polymers* (Ed: B. Scrosati), Chapman and Hall, London **1993**, p. 150.

[201] T. Iyoda, A. Ohtani, T. Shimidzu, K. Honda, *Synth. Met.* **1987**, *18*, 725.

[202] C. Barbero, M. C. Miras, B. Schnyder, O. Haas, R. Kotz, *J. Mater. Chem.* **1994**, *4*, 1775.

[203] H. K. Youssoufi, F. Garnier, A. Yassar, S. Baiteche, P. Srivastava, *Adv. Mater.* **1994**, *6*, 755.

[204] T. Iyoda, A. Ohtani, T. Shimidzu, K. Honda, *Synth. Met.* **1987**, *18*, 747.

[205] T. Shimidzu, A. Ohtani, T. Iyoda, K. Honda, *J. Electroanal. Chem. Interfacial Electrochem.* **1987**, *224*, 123.

[206] R. Gangopadhyay, A. De, *Chem. Mater.* **2000**, *12*, 608.

[207] S. Holdcroft, B. L. Funt, *J. Electroanal. Chem. Interfacial Electrochem.* **1988**, *240*, 89.

[208] C. S. C. Bose, K. Rajeshwar, *J. Electroanal. Chem.* **1992**, *333*, 235.

[209] H.-S. Li, M. Josowicz, M. Engelhard, D. R. Baer, J. Janata, *Proc. Electrochem. Soc.* **1994**, *94–14*, 123.

[210] K. Rajeshwar, C. S. C. Bose, *US Patent 5 334 292*, **1994**.

[211] K. Rajeshwar, C. Wei, W. Wampler, C. S. C. Bose, S. Basak, S. German, D. Evans, V. Krishna, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35*, 234.

[212] W. A. Wampler, C. Wei, K. Rajeshwar, *J. Electrochem. Soc.* **1994**, *141*, L13.

[213] W. A. Wampler, C. Wei, K. Rajeshwar, *Chem. Mater.* **1995**, *7*, 585.

[214] W. A. Wampler, K. Rajeshwar, R. G. Pethe, R. C. Hyer, S. C. Sharma, *J. Mater. Res.* **1995**, *10*, 1811.

[215] W. A. Wampler, S. Basak, K. Rajeshwar, *Carbon* **1996**, *34*, 747.

[216] G. A. Sotzing, J. N. Phend, R. H. Grubbs, N. S. Lewis, *Chem. Mater.* **2000**, *12*, 593.

[217] N. S. Lewis, C. Lewis, R. Grubbs, G. A. Sotzing, *Int. Patent Appl. WO 2000 020 852 A1*, **2000**.

[218] E. Genies, *French Patent FR 2 591 605 A1*, **1987**.

[219] G. Bidan, O. Jarjayes, J. M. Fruchart, E. Hannecart, *Adv. Mater.* **1994**, *6*, 152.

[220] M. Wan, W. Zhou, J. Li, *Synth. Met.* **1996**, *78*, 27.

[221] H. Yoneyama, A. Kishimoto, S. Kuwabata, *J. Chem. Soc., Chem. Commun.* **1991**, *15*, 986.

[222] H. Yoneyama, *Japanese Patent JP 04 136 195 A2*, **1992**.

[223] S. Kuwabata, A. Kisimoto, T. Tanaka, H. Yoneyama, *J. Electrochem. Soc.* **1994**, *141*, 10.

[224] C.-L. Huang, R. E. Partch, E. Matijevic, *J. Colloid Interface Sci.* **1995**, *170*, 275.

[225] M. Matsumura, T. Ohno, S. Saito, M. Ochi, *Chem. Mater.* **1996**, *8*, 1370.

[226] K. Murakoshi, R. Kogure, Y. Wada, S. Yanagida, *Chem. Lett.* **1997**, *5*, 471.

[227] M. Matsumura, T. Ohno, *Adv. Mater.* **1997**, *9*, 357.

[228] A. C. Arango, P. J. Brock, S. A. Carter, *Mater. Res. Soc. Symp. Proc.* **1999**, *561*, 149.

[229] A. C. Arango, S. A. Carter, P. J. Brock, *Appl. Phys. Lett.* **1999**, *74*, 1698.

[230] H. Yoneyama, Y. Shoji, *J. Electrochem. Soc.* **1990**, *137*, 3826.

[231] H. Yoneyama, S. Hirao, S. Kuwabata, *J. Electrochem. Soc.* **1992**, *139*, 3141.

[232] P. K. Shen, H. T. Huang, A. C. C. Tseung, *J. Electrochem. Soc.* **1992**, *139*, 1840.

[233] B. P. Jelle, G. Hagen, S. Noedland, *Electrochim. Acta* **1993**, *38*, 1497.

[234] N. R. Avvaru, N. R. de Tacconi, K. Rajeshwar, *Analyst* **1998**, *123*, 113.

[235] S. Maeda, S. P. Armes, *Synth. Met.* **1995**, *73*, 151.

[236] S. Maeda, S. P. Armes, *Chem. Mater.* **1995**, *7*, 171.

[237] M. D. Butterworth, R. Corradi, J. Johal, S. F. Sascelles, S. Maeda, S. P. Armes, *J. Colloid Interface Sci.* **1995**, *174*, 510.

[238] K. Jackowska, H. T. Tien, *J. Appl. Electrochem.* **1988**, *18*, 357.

[239] K. Jackowska, M. Skompska, *Electrocatal.* **1988**, *Mater. Symp. Electrochem. Sect. Pol. Chem. Soc.*, 9th.

[240] K. Jackowska, M. Skompska, *Polym. J. Chem.* **1990**, *64*, 657.

[241] H. Yoneyama, M. Tokuda, S. Kuwabata, *Electrochim. Acta* **1994**, *39*, 1315.

[242] M. Lal, M. Joshi, D. N. Kumar, C. S. Friend, J. Winiarz, T. Asefa, K. Kim, P. N. Prasad, *Mater. Res. Soc. Symp. Proc.* **1998**, *519*, 217.

[243] P. Chartier, H. Nguyen Cong, C. Sene, *Sol. Energy Mater. Sol. Cells* **1998**, *52*, 413.

[244] M. G. Kanatzidis, C. G. Wu, H. O. Marcy, C. R. Kannewurf, *J. Am. Chem. Soc.* **1989**, *111*, 4139.

[245] C. G. Wu, M. G. Kanatzidis, H. O. Marcy, D. C. DeGroot, C. R. Kannewurf, *NATO ASI Ser. B* **1990**, 248.

[246] C. G. Wu, H. O. Marcy, D. C. DeGroot, C. R. Kannewurf, M. G. Kanatzidis, *Mater. Res. Soc. Symp. Proc.* **1990**, *173*, 317.

[247] M. G. Kanatzidis, C. G. Wu, Y. J. Liu, D. C. DeGroot, J. L. Schindler, H. O. Marcy, C. R. Kannewurf, *Mater. Res. Soc. Symp. Proc.* **1991**, *233*, 183.

[248] V. D. Pokhodenko, V. G. Koshechko, V. A. Krylov, *J. Power Sources* **1993**, *45*, 1.

[249] Y. J. Liu, D. C. DeGroot, J. L. Schindler, C. R. Kannewurf, M. G. Kanatzidis, *J. Chem. Soc., Chem. Commun.* **1993**, *7*, 593.

[250] T. Fujii, N. Katagiri, O. Kimura, T. Kabata, Y. Kurosawa, Y. Hayashi, H. Iechi, T. Ohsawa, *Synth. Met.* **1995**, *71*, 2225.

[251] H. Nakajima, G.-E. Matsubayashi, *J. Mater. Chem.* **1995**, *5*, 105.

[252] F. Leroux, B. E. Koene, F. L. Nazar, *J. Electrochem. Soc.* **1996**, *143*, L181.

[253] C. G. Wu, D. C. DeGroot, H. O. Marcy, J. L. Schindler, C. R. Kannewurf, Y. J. Liu, W. Hirpo, M. G. Kanatzidis, *Chem. Mater.* **1996**, *8*, 1992.

[254] F. Leroux, G. Goward, W. P. Power, L. F. Nazar, *J. Electrochem. Soc.* **1997**, *144*, 3886.

[255] M. Lira-Cantú, *Ph.D. Thesis*, University Autonoma de Barcelona **1997**, p. 245.

[256] S. Kuwabata, T. Idzu, C. R. Martin, H. Yoneyama, *J. Electrochem. Soc.* **1998**, *145*, 2707.

[257] M. Lira-Cantu, P. Gomez-Romero, *J. Electrochem. Soc.* **1999**, *146*, 2029.

[258] M. Lira-Cantu, P. Gomez-Romero, *J. New Mater. Electrochem. Syst.* **1999**, *2*, 141.

[259] M. Lira-Cantu, G. Torres-Gomez, P. Gomez-Romero, *Mater. Res. Soc. Symp. Proc.* **1999**, *548*, 367.

[260] M. Lira-Cantu, P. Gomez-Romero, *J. Solid State Chem.* **1999**, *147*, 601.

[261] D. C. DeGroot, J. L. Schindler, C. R. Kannewurf, Y. J. Liu, C. G. Wu, M. G. Kanatzidis, *Mater. Res. Soc. Symp. Proc.* **1992**, *274*, 133.

[262] B. C. Dave, B. S. Dunn, F. Leroux, L. F. Nazar, H. P. Wong, *Mater. Res. Soc. Symp. Proc.* **1996**, *435*, 611.

[263] B. C. Dave, B. Bunn, F. Leroux, L. F. Nazar, H. P. Wong, *Report* **1996**, *Order No. AD-A310639*, p. 8. Avail. NTIS from: Gov. Rep. Announce. Index.

[264] J. H. Harreld, B. Dunn, W. Cheng, F. Leroux, L. F. Nazar, *Mater. Res. Soc. Symp. Proc.* **1998**, *519*, 191.

[265] H. P. Wong, B. C. Dave, F. Leroux, J. Harreld, B. Dunn, L. F. Nazar, *J. Mater. Chem.* **1998**, *8*, 1019.

[266] M. G. Kanatzidis, C. G. Wu, H. O. Marcy, D. C. DeGroot, C. R. Kannewurf, *Chem. Mater.* **1990**, *2*, 222.

[267] G. R. Goward, F. Leroux, L. F. Nazar, *Electrochim. Acta* **1998**, *43*, 1307.

[268] L. F. Nazar, X. T. Yin, D. Zinkweg, Z. Zhang, S. Liblong, *Mater. Res. Soc. Symp. Proc.* **1991**, *210*, 417.

[269] L. F. Nazar, Z. Zhang, D. Zinkweg, *J. Am. Chem. Soc.* **1992**, *114*, 6239.

[270] L. F. Nazar, T. Kerr, B. Koene, in *Access in Nanoporous Materials* (Eds: T. J. Pinnavia, M. F. Thorpe), Fundamental Materials Science Series, Kluwer, Dordrecht, The Netherlands **1995**, p. 405.

[271] P. G. Hill, P. J. S. Foot, R. Davis, *Mater. Sci. Forum* **1995**, *191*, 43.

[272] P. G. Hill, P. J. S. Foot, R. Davis, *Synth. Met.* **1996**, *76*, 289.

[273] T. A. Kerr, F. Leroux, L. F. Nazar, *Chem. Mater.* **1998**, *10*, 2588.

[274] M. G. Kanatzidis, R. Bissessur, D. C. DeGroot, J. L. Schindler, C. R. Kannewurf, *Chem. Mater.* **1993**, *5*, 595.

[275] R. Bissessur, J. L. Schindler, C. R. Kannewurf, M. Kanatzidis, *Mol. Cryst. Liq. Cryst. Sci. Technol. A* **1994**, *245*, 249.

[276] L. Wang, J. Schindler, J. A. Thomas, C. R. Kannewurf, M. G. Kanatzidis, *Chem. Mater.* **1995**, *7*, 1753.

[277] a) L. Wang, P. Brazis, M. Rocci, C. R. Kannewurf, M. G. Kanatzidis, *Mater. Res. Soc. Symp. Proc.* **1998**, *519*, 257. b) L. Wang, M. Rocci-Lane, P. Brazis, C. R. Kannewurf, Y.-I. Kim, W. Lee, J.-H. Choy, M. G. Kanatzidis, *J. Am. Chem. Soc.* **2000**, *122*, 6629.

[278] M. G. Kanatzidis, H. O. Marcy, W. J. McCarthy, C. R. Kannewurf, T. J. Marks, *Solid State Ionics* **1989**, *32–33*, 594.

[279] M. G. Kanatzidis, M. Hubbard, L. M. Tonge, T. J. Marks, H. O. Marcy, C. R. Kannewurf, *Synth. Met.* **1989**, *28*, C89.

[280] M. G. Kanatzidis, C. G. Wu, H. O. Marcy, D. C. DeGroot, C. R. Kannewurf, A. Kostikas, V. Papaefthymiou, *Adv. Mater.* **1990**, *2*, 364.

[281] C. G. Wu, H. O. Marcy, D. C. DeGroot, J. L. Schindler, C. R. Kannewurf, W. Y. Leung, M. Benz, E. LeGoff, M. G. Kanatzidis, *Synth. Met.* **1991**, *41*, 797.

[282] K. Prassides, C. J. Bell, A. J. Dianoux, C. G. Wu, M. G. Kanatzidis, *Physica B* **1992**, *180–181*, 668.

[283] M. G. Kanatzidis, C. G. Wu, H. O. Marcy, D. C. DeGroot, J. L. Schindler, C. R. Kannewurf, M. Benz, E. LeGoff, *ACS Symp. Ser.* **1992**, *499*, 194.

[284] M. G. Kanatzidis, C. G. Wu, D. C. DeGroot, J. L. Schindler, M. Benz, E. LeGoff, C. R. Kannewurf, *NATO ASI Ser. B* **1993**, 305.

[285] E. Ruiz-Hitzky, P. Aranda, *An. Quim. Int. Ed.* **1997**, *93*, 197.

[286] A. Destefanis, S. Foglia, A. A. G. Tomlinson, *J. Mater. Chem.* **1995**, *5*, 475.

[287] Y. J. Liu, M. G. Kanatzidis, *Inorg. Chem.* **1993**, *32*, 2989.

[288] T. Bein, P. Enzel, *NATO ASI Ser. E* **1993**, 246.

[289] L. Zuppiroli, F. Beuneu, J. Mory, P. Enzel, T. Bein, *Synth. Met.* **1993**, *57*, 5081.

[290] C. G. Wu, T. Bein, *Science* **1994**, *264*, 1757.

[291] C. G. Wu, T. Bein, *Chem. Mater.* **1994**, *6*, 1109.

[292] C. G. Wu, T. Bein, *Stud. Surf. Sci. Catal.* **1994**, *84*, 2269.

[293] T. Bein, *Stud. Surf. Sci. Catal.* **1996**, *102*, 295.

[294] A. G. Pattantyus-Abraham, M. O. Wolf, *Mater. Res. Soc. Symp. Proc.* **1999**, *560*, 291.

[295] K. Otsuka, S. Osada, *Jpn. Patent Jpn. Kokai Tokkyo Koho JP 62 290 759 A2*, **1987**.

[296] O. Ikeda, H. Yoneyama, *J. Electroanal. Chem.* **1989**, *265*, 323.

[297] N. Leventis, Y. C. Chung, *J. Electrochem. Soc.* **1990**, *137*, 3321.

[298] A. A. Karyakin, M. F. Chaplin, *J. Electroanal. Chem.* **1994**, *370*, 301.

[299] M. Morita, *J. Appl. Polym. Sci.* **1994**, *52*, 711.

[300] K. Ogura, N. Endo, M. Nakayama, H. Ootsuka, *J. Electrochem. Soc.* **1995**, *142*, 4026.

[301] K. Ogura, N. Endo, M. Nakayama, *J. Electrochem. Soc.* **1998**, *145*, 3801.

[302] J. Livage, N. Gharbi, M. C. Leroy, M. Michaud, *Mater. Res. Bull.* **1978**, 1117.

[303] J. Livage, *Chem. Mater.* **1991**, *3*, 578.

[304] D. Curran, J. Grimshaw, S. D. Perera, *Chem. Soc. Rev.* **1991**, *20*, 391.