

## REVIEW ARTICLE

# Application of Hybrid Polymeric Complexes to Solid State and Materials Chemistry

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**ABSTRACT.** A bird's-eye view on preparation, structure and properties of polymeric complexes in the field of Inorganic-Organic-Hybrids is presented in the view point of solid state and materials chemistry. These materials are useful precursors for preparing nanoparticles and fine grain oxides. Some of them are electroactive and are used as protonic or lithium electrolytes, electrochromic materials or membranes for sensors and actuators. New results on bio-hybrids, a class of material not far from polymeric complexes, are also described.

## INTRODUCTION

A hybrid is literally defined as «a thing composed of incongruous elements», but in the field of chemistry, the word «hybrid» is not clearly defined. It is generally applied to solid materials, made of organic groups together with inorganic cations or anions with a polymeric organization. A more precise definition is IOH, acronym for Inorganic-Organic-Hybrid.

The contemporary deep interest for these materials is due to various reasons which are either of rational or of irrational order. From a rationalistic point of view, an obvious advantage of hybrids is that they favorably combine the properties of organic materials to that of inorganic ones. Consequently this field appears to be very creative providing an opportunity to invent an almost unlimited set of new compounds with a large spectrum of known or unknown properties. Due to their hybrid constitution, one can speculate the formation of new multifunctional materials. As a consequence of this multifunctionality, this area is also a good field for scouting «smart materials».

As hybrids are in general polymeric materials,

they inherit the general properties of polymers. For example, in the case of mechanical properties, they are «soft» compared to the most of inorganic materials; as a consequence, they could be easily shaped in any form, bulk or film. If they are non-crystalline and transparent in the visible region, they could be applied to many optical devices.

One observes that, since last century, the soft polymeric materials tend to replace the hard metallic or inorganic compounds in the day-to-day life. There are, of course, some pragmatic reasons for that evolution. For instance, polymeric materials are lighter than inorganic ones and consequently more adaptable to the modern man who is, in essence, more and more nomadic and prefers tiny and lighter objects to move easily.

In fact, a deep interest for IOH arises from irrational reasons which belong to a «collective unconsciousness». De Gennes<sup>1</sup> suggests that this fascination for the «fragile» polymeric solids is due to their similarity with biological materials constituting our body. This analogy is even greater for hybrids because the biological soft part of body contains both organic matter and inorganic oligo-elements.

## A BIRD'S-EYE VIEW ON POLYMERIC COMPLEXES IN THE FIELD OF INORGANIC-ORGANIC-HYBRIDS

The prefix inorganic-organic associated with the word «hybrid» is not sufficient to clarify the subject of IOH. Indeed, many materials can be qualified as IOH. So, it seems also necessary to add a suffix to «hybrid» to identify these materials.

Many types of polymeric materials can be designated as hybrids: ORMOCER, ionomers, polymeric salts or complexes, etc.. The previous list is not exhaustive but for the sake of clarity, let us outline only some of them.

### Monophasic Hybrids

**ORMOCER (IOH-sg).** ORMOCER's (Organic Modified Ceramic) called also ORMOSIL (Organic Modified Silicates) are constituted by an inorganic backbone, generally tridimensional onto which organic groups are attached. These materials are produced by sol-gel chemistry (Fig. 1).<sup>2</sup>

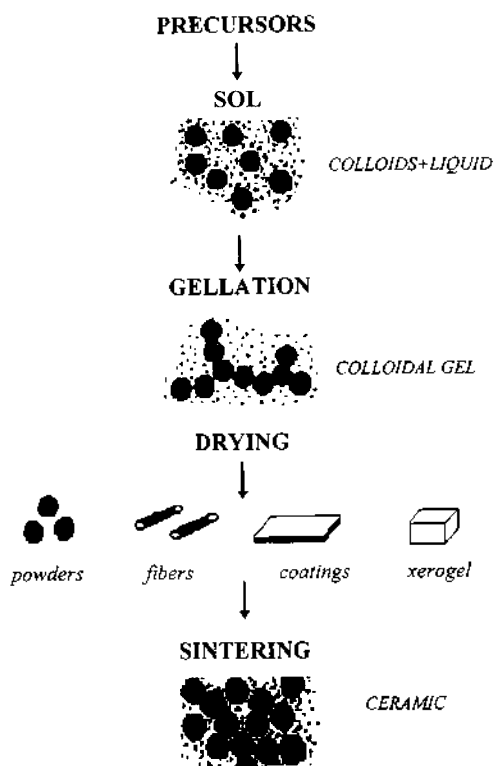


Fig. 1. Simplified diagram of material processing by sol-gel route.<sup>2</sup>

As recently reviewed by Judeinstein and Sanchez<sup>3</sup> or by Chujo<sup>4</sup>, these materials can be produced by controlled hydrolysis and polycondensation of organic precursors, generally alkoxides (Fig. 2).<sup>5</sup> For example, there are various intracrystalline grafting of n-alkylsilane on silicic acids, which are formed by hydrolysis of chlorosilanes. Polysiloxanes, which are commercially available at a large scale, are the most familiar IOH-sg.

**Ionomers (IOH-i).** These polymers can be considered as salts resulting from the neutralization of polyacids or polybases. The most common ionomers are the salts arising from the neutralization of sulfonic acids by an inorganic base. As an example, one can quote NAFION<sup>®</sup> in which the proton of sulfonyl group can be exchanged by various cations including alkali metal ions.

**Polymeric Salts or Complexes (IOH-cc).** These materials result from the complexation reaction between polymers possessing basic groups and inorganic cations, which are sometimes improperly called polymer salt. In order to avoid a confusion with ionomers that are really salts, they will be named as IOH-cc, (Inorganic-Organic-Hybrid-Co-ordination Complex) hereafter.

The first material was discovered in 1964 by Blumberg *et al.*,<sup>7</sup> who isolated the complex  $-(\text{CH}_2\text{CH}_2\text{O})_4\text{HgCl}_2-$ . They became very popular after 1973 when Fenton *et al.*<sup>8</sup> discovered the solubility of alkali salts in PEO [poly(ethylene oxide)] and in 1979 when Armand *et al.* proposed to use this material as solid electrolyte in batteries.<sup>9</sup> Recently, it was also found that the complexation of metal salt and polyol medium can be effectively utilized to produce fine metal particles.<sup>10,11</sup>

**Conducting Polymers (IOH-ecp).** Some electr-

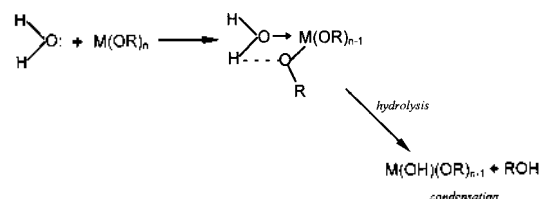


Fig. 2. Hydrolysis and polycondensation of alcoholates.<sup>5</sup>

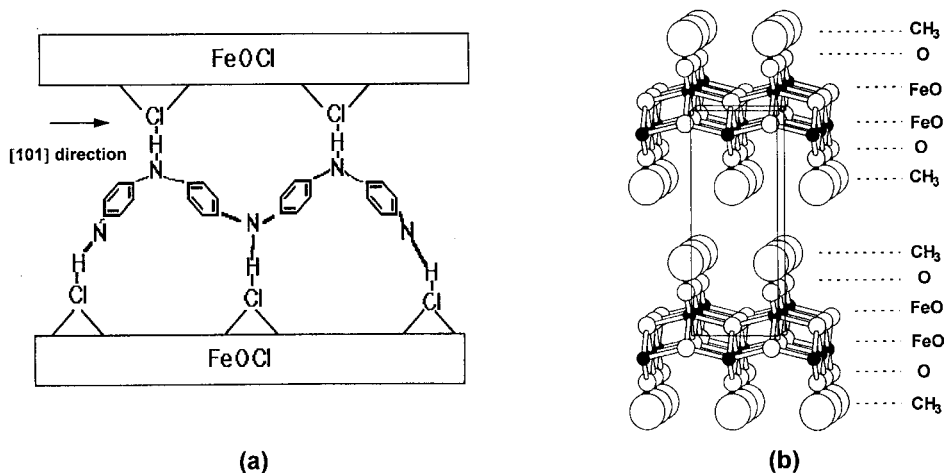


Fig. 3. (a) Intercalated polyaniline in FeOCl lattice (b) Methoxy-substituted FeOCl derivative.

onic conducting polymers are produced by electropolymerisation in the presence of inorganic species.<sup>12,13</sup>

**Low Dimensional Hybrids (IOH-ld).** A new class of hybrids has been recently discovered, so called low dimensional hybrids (IOH-ld). The backbone of these materials is an inorganic solid (oxide, sulphide, oxychloride, ...) with a lamellar or tunnel structure into which a polymer is inserted.

Since the pioneering work by Hagemuller *et al.*,<sup>14</sup> it is well known that MOCl (M=Fe, Ti, and V) can intercalate amines.<sup>15,16</sup> One can also mention other derivatives from FeOCl, which are polyaniline intercalated (Fig. 3(a))<sup>17</sup> or methoxy-substituted one (Fig. 3(b)).<sup>18</sup> Readers can fruitfully consult the review paper by O'Hare.<sup>19</sup>

More recently, the intercalation of high tem-

perature superconductors  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$  ( $n=1, 2$ , and  $3$ )<sup>20-27</sup> have been intensively studied for the application purpose or the understanding of superconducting mechanism. Choy *et al.* reported that electronic conducting-insulating<sup>21-24</sup> or electronic-ionic mixed conducting nano hybrids,<sup>25-27</sup>  $\text{M-X-Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$  (M=Hg, Ag, X=Br, I) can be constructed. Among them, the latter mixed conductors, Ag-I- $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$  could be promising materials for the electrode applications in various electrochemical devices. Further, they provided a possible route to the fabrication of superconducting thin film by intercalating organic moiety into the  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$  lattice (Fig. 4).<sup>28,29</sup>

#### Polyphasic Hybrids

**Swollen Polymers (IOH-sp).** Some polymer

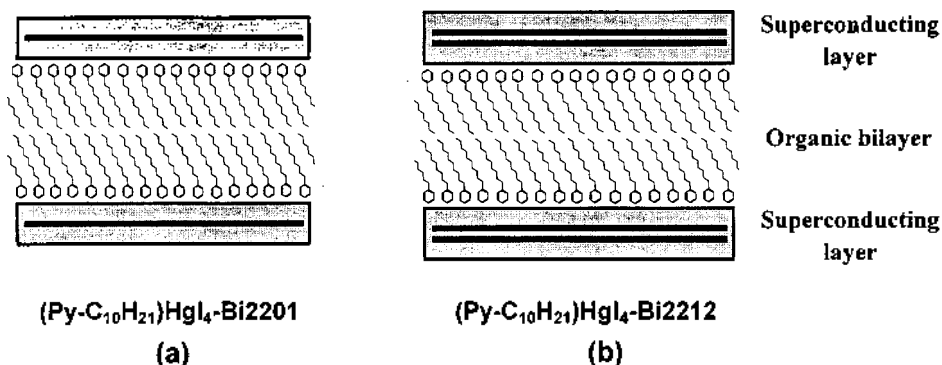


Fig. 4. Schematic structure model for (a)  $(\text{Py-C}_{10}\text{H}_{21})\text{HgI}_4\text{-Bi2201}$  and (b)  $(\text{Py-C}_{10}\text{H}_{21})\text{HgI}_4\text{-Bi2212}$ .

cannot bind inorganic salts because there is a conflict between the basicity of basic groups in polymer and the acidity of cation to be bound. In this case, it is sometimes possible to create a hybrid by using a solvent that dissolves inorganic salt as well as the polymer. These IOH-sp have similar properties with IOH-cc (see § 5). As an example, one can refer to, hybrid films composed of polyacrylonitrile, ethylene carbonate and  $\text{LiClO}_4$ .<sup>45-47</sup>

**Solid-solid Composite (IOH-ssc).** Composite or nanocomposite are «hybrid» in nature. Obviously any polymer or hybrid can be mixed with a solid matter to form a composite. Some examples will be shown in § 5. One example, as proposed by Skaarup *et al.*, is a Li conductive glass based on  $\text{Li-Li}_2\text{S-B}_2\text{S}_3$  mixed with nonconductive PEO.<sup>48</sup> Nanoparticles embedded in a polymer can be also considered as IOH-ssc (see § 5).

#### Comparison of IOH-sg and IOH-cc

At the present time, in solid state chemistry, most of the research on hybrids are devoted to sol-gel chemistry (IOH-sg). It can be interesting to compare xerogel hybrids produced by the sol-gel route and polymeric complexes.

In IOH-sg, the polymeric sublattice is generally inorganic, and its structure is tridimensional. The metal-oxygen bond is covalent (Si-O-Si, Sn-O-Sn,

Zr-O-Zr, ...); the organic groups are also covalently bound to the inorganic framework. On the contrary, in the case of IOH-cc, polymeric sublattice is organic, basically monodimensional, while inorganic cations are coordinatively bound to polymer.

## PREPARATION

The formation of IOH-cc results from a Lewis acid-base reaction between coordinating group of polymer and inorganic cation. Many functions can be used for such a bond. Some examples are listed in Table 1. Roughly speaking, the formula of the obtained hybrid, expressed by the ratio R (=monomer/salt) depends on several factors:

*the relative strengths of basic active group of polymer and of the acidity of cation*

*the coordination number of cation*

In the case of polyamides and  $\text{GaCl}_3$ , a 1:1 complex could be formed, in which each amide group is bound to a  $\text{GaCl}_3$  species leading to a four coordinated gallium.<sup>44</sup> For the complex between poly(ethylene oxide) and  $\text{LiClO}_4$ , the ratio R is greater than ten (Fig. 5).

Other factors are important. The lattice energy of the salt has to be low to avoid coagulation during the forming process.<sup>49</sup> The anion of organic

Table 1. Some polymeric complexes

Polymer	Inorganic	Ref.
Poly(vinyl alcohol)	$\text{LiBF}_4$	30
Poly(vinyl alcohol)	$\text{H}_3\text{PO}_4$	31
Poly(acrylic acid)	Y, Cu, Ba nitrates	32
Poly(ethylene oxide)	$\text{LiClO}_4$	9
Nylon Elvamide 8061	$\text{MX}_n$ ; $\text{M}^{n+}=\text{Li}^+, \text{Zn}^{2+}, \text{Fe}^{3+}$ , $\text{X}=\text{Cl}^-, \text{Br}^-$	33
Poly(acryl amide)	$\text{CdX}_2$ ( $\text{X}=\text{Cl}, \text{Br}$ )	34
Poly(acryl amide)	$\text{H}_3\text{PO}_4$	35, 36
Nylon 6	$\text{FeCl}_3$	37
Poly(ethylene oxide)	$\text{RbAg}_4\text{I}_5$	38
Poly(vinyl alcohol)	$\text{CuSO}_4$ , $\text{Cu}(\text{NO}_3)_2$ , $\text{CuBr}_2$	39
Poly(acryl amide)	$\text{CuSO}_4$ , $\text{Cu}(\text{NO}_3)_2$ , $\text{CuBr}_2$	39
Poly(acryl amide + acrylic acid)	$\text{TbCl}_3$	40
Poly(acryl amide)	$\text{BiCl}_3$ , $\text{BiI}_3$	41
Poly(acryl amide + ethylene oxide)	$\text{LiClO}_4$	42
Poly(methyl methacrylate + propylene glycol)	$\text{LiCF}_3\text{SO}_3$	43
Polyamides	$\text{GaCl}_3$	44
etc.	etc.	

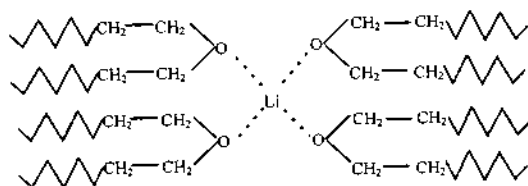


Fig. 5. Schematic structure of PEO-LiClO<sub>4</sub>.

salt may also play an important role.

The preparation of IOH-cc can be made by two ways: i) by simple addition reaction in solution, where a polymer is dissolved with an inorganic salt in a common solvent, ii) by copolymerisation of a monomer with an inorganic salt.

The first process is particularly simple. One uses a solvent in which both polymer and inorganic salt are soluble (Table 2). Then the solvent is partially or totally evaporated. In the first situation, a polymeric gel is obtained whose viscosity depends on the proportion of remaining solvent. When the solvent is completely evaporated, one obtains a film with plastic mechanical properties.

The other process consists of two steps; at first a monomeric complex is prepared, and then polymerized. At the first glance, it seems to be identical to the previous process. In fact some authors claim that the homogeneity of materials obtained by such a copolymerisation is better than that by the simple addition reaction in solution.<sup>32</sup>

Of course, the polymeric organic part of hybrid can be more sophisticated. For example, copolymers can be used; a combination often encountered in aqueous solution is copolymer of acrylamide and acrylic acid.<sup>40,41</sup> Polymer blend can be used like poly(methyl methacrylate) and poly

(propylene glycol),<sup>48</sup> poly(ethylene oxide) and poly(methyl methacrylate), etc..

## STRUCTURE

Obviously, the problem of crystallinity of IOH-cc, is not drastically different from that of organic polymer. That is to say, these materials can be crystalline, non-crystalline or semi-crystalline. However, as it will be shown later, the introduction of an organic salt in polymer usually leads very often to a cross-linking of the polymer chains. Consequently an extra kinetic effect prevents the crystallization so that IOH-cc are generally non-crystalline, at least until the precipitation of salt occurs giving rise to the formation of a composite. Being simultaneously amorphous and possessing a  $T_g$ , they can be considered as «hybrid glass», which is in agreement with the definition of vitreous state.<sup>53</sup>

However, the structures of some crystalline IOH-cc have been previously determined by X-ray diffraction, as in the cases for the complex formed between NaI and poly(ethylene oxide), (EO)<sub>3</sub>NaI<sup>54</sup> or the one formed between the same polymer and HgCl<sub>2</sub>, (EO)<sub>4</sub>·HgCl<sub>2</sub>.<sup>55</sup>

The structural organization of IOH-cc can be divided into several types depending on i) the number of polymeric chains involved in the complexation of inorganic part, and ii) the dismutation or non dismutation of inorganic groups.

In the case of complexes obtained from poly(ethylene oxide) and lithium salts, it has been proposed that only one polymeric chain is involved, the coordination of lithium being obtained by a

Table 2. Some associations polymer-inorganic salt-solvent

Polymer	Solvent	Inorganic salt	Ref.
Poly(acryl amide)	H <sub>2</sub> O	BiCl <sub>3</sub>	41
Poly(ethylen oxide)	CH <sub>3</sub> CN	WCl <sub>6</sub> , SnCl <sub>4</sub>	50
Poly(methyl metacrylate)	(CH <sub>3</sub> ) <sub>2</sub> CO	BiI <sub>3</sub>	51
Poly(ethylen oxide)	CH <sub>3</sub> CH <sub>2</sub> OH	TiCl <sub>4</sub>	52
Nylon6	HCOOH	FeCl <sub>3</sub>	37
Elvamide 8061	CH <sub>3</sub> OH	LiCl, LiBr, ZnCl <sub>2</sub>	33
Poly(vinyl alcohol)	H <sub>2</sub> O	CuSO <sub>4</sub>	39

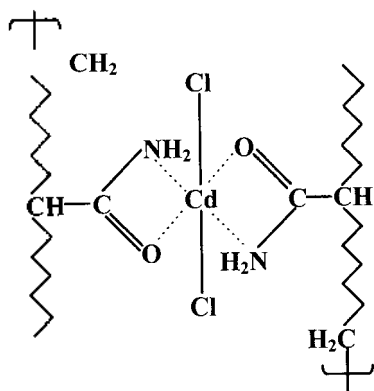


Fig. 6. Schematic structure of PAam-CdCl<sub>2</sub>.

chain bending adopting a ring type shape. Now, it is known that in fact intra or intermolecular complexation occurs at the same time.<sup>56</sup>

Generally speaking, the most common role of inorganic part is to lead to a cross-linking between polymeric chains. It is the case for the hybrid poly(acrylamide·0.5CdCl<sub>2</sub>) in which every cadmium is complexed to two amide groups belonging to two different chains. According to the vibrational spectroscopic studies, it seems that the main bond between polymer and chloride is insured via the carbonyl group, corresponding to a four coordination (CO)<sub>2</sub>CdCl<sub>2</sub> or a pseudo six coordination (CONH<sub>2</sub>)<sub>2</sub>CdCl<sub>2</sub> for the cadmium ion (Fig. 6).<sup>34</sup>

Some more complex structures have been also observed especially in the case of transition elements. For example, Nylon-6 gives a complex

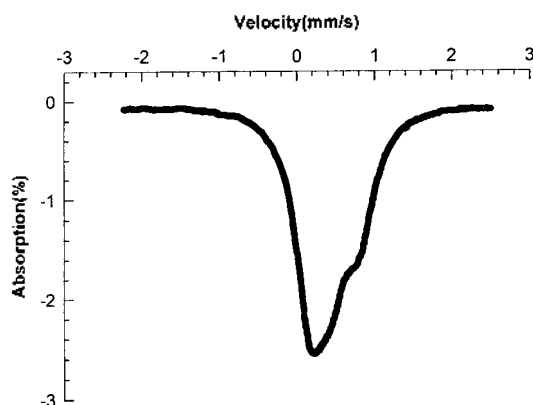


Fig. 7. Mössbauer spectrum of Nylon6-FeCl<sub>3</sub> hybrid.

with FeCl<sub>3</sub> (CONH/FeCl<sub>3</sub>=3). In this complex, a part of the iron is in the form Fe(L'<sup>4</sup>)Cl<sub>2</sub><sup>+</sup> inside the polymer and the other part in the anionic form FeCl<sub>4</sub><sup>-</sup> between chains. This fact is illustrated by Mössbauer spectroscopy that clearly shows the existence of two types of Fe<sup>3+</sup> (Fig. 7).<sup>37</sup>

## APPLICATIONS IN MATERIALS CHEMISTRY

The polymeric complexes can be used directly for their own properties or as precursors for the preparation of various materials.

### IOH-cc as Precursors

**Nanocomposites.** Nowadays nanoparticles, based on isolated colloidal particles with few nanometers in a matrix are widely studied. This size effect produces new properties. In the case of semiconductors, there is a quantum confinement of charge carriers leading to a shift of the band gap energy.

IOH-cc constitutes an appropriate medium to prepare such materials. The process consists of two steps; at first the polymeric complex is prepared, and then it reacts with a compound leading to a precipitation. Due to the high viscosity of the medium large crystallites cannot be easily grown up, so that nanoparticles are produced inside the polymer giving rise to the formation of nanocomposite.

Many publications are devoted to this subject and it is difficult to give a detailed view here. One can mention the preparation of X-ray photoconductive nanocomposites made of BiI<sub>3</sub> in Nylon-11.<sup>57</sup> The same photoconductive bismuth iodide can be also introduced in poly(acryl amide) (PAam).<sup>58</sup> The complex PAam-CdCl<sub>2</sub>,<sup>34</sup> washed with ammonium sulphide dilute solution leads to a PAam-CdS nanocomposite in which the particle size is about 3 nm.<sup>59</sup> Optically transparent poly(methyl methacrylate) films incorporated by CdS quantum crystallites have been prepared.<sup>60</sup> The preparation of nanocomposites consisting of (MoSe<sub>3</sub>)<sub>n</sub> nanowires in poly(vinylene carbonate) has been also reported.<sup>61</sup> Divalent copper complexes with poly(vinyl alcohol) or poly(acryl amide) treated by iodine lead to a semiconducting film by formation of polymers-CuI.<sup>62</sup>

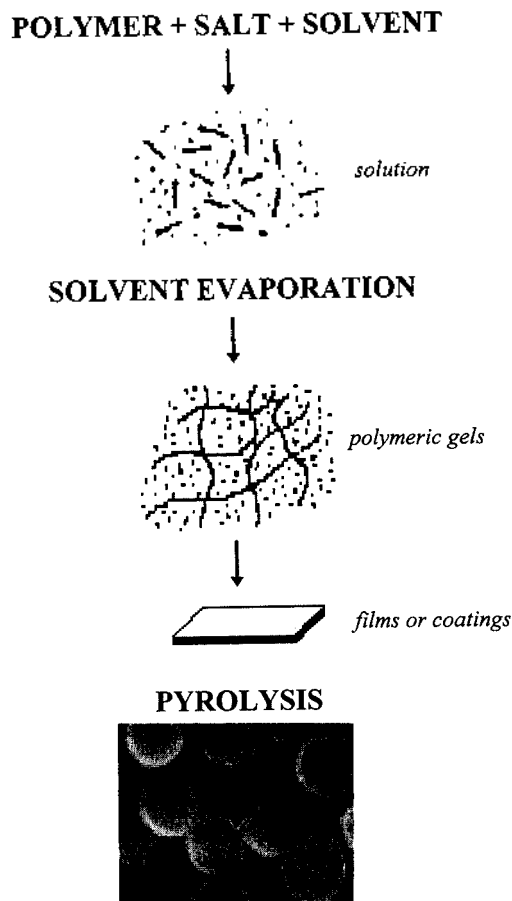


Fig. 8. Simplified flow chart of oxide synthesis by IOH-cc route.

**Preparation of Fine Powders.** For some devices or applications, it is sometimes important to have small particles.<sup>63-75</sup> It is the case for electrode materials used in batteries, catalysts, etc.. IOH-cc can be used as precursors for such purposes.

The general process is suggested on Fig. 8. It is very close to sol-gel processes. Instead of starting from an alkoxide as precursor, one can advantageously use a polymeric complex: the number of metallic alkoxide is indeed limited whereas the collection of IOH-cc is almost infinite. In addition, in the case of synthesis of multicomponent oxides, the sol-gel processes (or classical coprecipitation) are not always effective in maintaining reactant distribution during hydrolysis or heating.<sup>76</sup>

One can consider the polymeric complex routes

that are derived from the combustion of oxalates, citrates, etc. (for example see ref 77 and 78 for the preparation of 1-2-3 superconductors). Since the use of a polymeric phase instead of a mixture of monomers seems more efficient in terms of homogeneity of the obtained oxides, the methods have been used in the preparation of fine ceramics as well as ionic conductor, dielectric materials, and ferrites up to the present.<sup>68-75</sup>

The first synthetic method, called the Pechini process,<sup>79</sup> has been initially designed to prepare titanates and niobates for dielectric uses. It is based on the property of weak acids to form chelates with cations. These chelates can undergo polyesterification when heated in a polyhydroxyl alcohol, to form a solid polymer. The Pechini process has been recently used for the preparation of  $\text{LiMn}_2\text{O}_4$ , positive electrode material.<sup>80</sup>

A similar but more simple method has been proposed for the preparation of High-Tc superconductor.<sup>32</sup> (Fig. 9) It simply uses the copolymerisation of acryl amide or acrylic acid with the corresponding metal nitrates involved in the final metal oxide. This method has been also used for preparing  $\text{LiMn}_2\text{O}_4$ .<sup>81</sup>

Poly(acryl amide) and iron nitrate react to give a hybrid  $\text{Aam} \cdot x\text{Fe}(\text{NO}_3)_3$  ( $0 < x < 0.25$ ). An explosive pyrolysis of this hybrid occurs at  $140^\circ\text{C}$  leading to  $\text{Fe}_2\text{O}_3$  with a specific surface area of  $2.7 \text{ m}^2/\text{g}$ . However, depending on the ratio PAam/nitrate, the resulting phase can be rich in polymer, whereas the magnetic phase is obtained for a high content of nitrate. It is an interesting result because ferrimagnetic iron sesquioxide is difficult to stabilize without doping.<sup>82</sup>

*CAUTION: the methods described in this paragraph have to be carefully used. Indeed, the mixing of reducing species like polymers (specially amides) and oxidizing species like nitrates could produce violent explosions. It is prudent to proceed to a prior test using small amounts of both components (less than 1g).*

### Electroactive Hybrids

Electroactive IOH-cc is probably the most studied. Indeed, it plays a significant role as a part of various electrochemical devices like solid state bat-

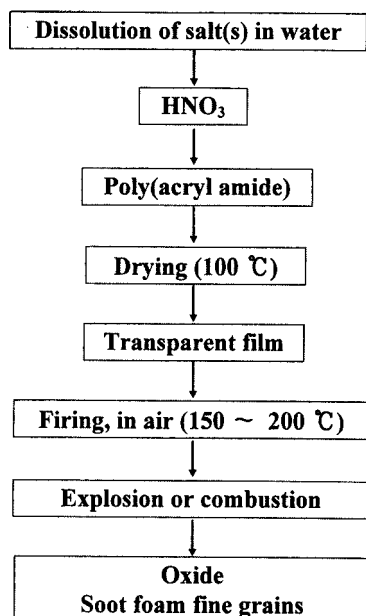


Fig. 9. Oxide preparation by internal oxido-reduction of nitrated.

teries, capacitors, electrochromic devices, chemical sensors or fuel cells. Therefore, the papers devoted to this subject are too abundant to present here an exhaustive survey. In this review, we outline only some general concepts together with some recent results obtained by us.

**Proton Conductors.** A general review on these materials can be found in reference 83. They can be used in electrochromic devices, capacitors or hydrogen-air fuel cells.

Basic polymers (polyethers, polyamines, polyalcohols, polyamides) blended with strong acids ( $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ , ...) give birth to solid proton electrolytes with a high conductivity at room temperature.<sup>84,85</sup> It is easy to make any shape with these materials as transparent thick films or thin films.

Some recent results are reported in Table 3. A conductivity of  $1.3 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$  is for a blend of poly(acryl amide) and poly(acrylic acid).

**Lithium Electrolytes.** The rapid advances in microelectronics permit to design new portable electronic devices. Power sources have to be simultaneously improved to provide electrical energy for these devices. One of the possible ways is to replace the conventional Ni-Cd or Ni-MH batteries by Li-ion rechargeable batteries, and the latter have been commercialized in Japan since 1990.

Liquid electrolytes were used for the first Li-ion batteries, but the requirement of a solid lithium electrolyte has been increasing rapidly: a solid but soft polymer electrolyte permits indeed the building of batteries with various shapes adaptable to the electronic devices.

Another important fact is that these batteries with liquid electrolyte are chemically and thermodynamically unstable, since the solvent like propylene carbonate for electrolytes could be often reduced by the lithium source (Li itself or Li intercalated in graphite). The interest of a solid electrolyte over a liquid one is to decrease the kinetic of electrochemical processes. Consequently solid batteries are safer.

Two types of hybrid have been developed for the application to solid electrolytes.<sup>86</sup> The first family is more or less issued from a pioneer work of Armand.<sup>9</sup> They corresponds to polymeric salts (IOH-cc) formed between a polymer (poly(ethylene oxide) and its derivatives for example) and a lithium salt ( $\text{LiClO}_4$ ,  $\text{LiPF}_6$ , etc.). However these electrolytes are not electrochemically stable above  $\sim 3.5 \text{ V}$  vs Li. The second group corresponds to swollen polymers (IOH-sp). A polymer, chosen for its electrochemical stability together with its mechanical properties, is

Table 3. Proton conductivity of some proton electrolytes<sup>85</sup> [PAam=poly(acryl amide); PAA=poly (acrylic acid)]

Polymer	% mol polymer	% mol additive	% mol $\text{H}_3\text{PO}_4$	Method	$\sigma(\Omega^{-1} \cdot \text{cm}^{-1})$
PAam	25	0	75	addition	$1.4 \times 10^{-3}$
PAam	25	0	75	copolymerisation	$1.7 \times 10^{-2}$
PAam	23	$2(\text{MgCl}_2 \cdot 6\text{H}_2\text{O})$	75	addition	$6.4 \times 10^{-3}$
PAA	25	0	75	addition	$2.1 \times 10^{-3}$
PAam	24	1.5 (PAA)	75	addition	$1.3 \times 10^{-2}$



Table 4.  $\text{Li}^+$  conductivity of hybrids based on poly (acrylonitrile) (PAN) swollen with ethylene carbonate (EC) and propylene carbonate (PC) as solvent of  $\text{LiPF}_6$ . (% mol.)

% PAN	% EC	% PC	% $\text{LiPF}_6$	$\sigma(20^\circ\text{C})$ ( $\Omega^{-1}\cdot\text{cm}^{-1}$ )
26	69.15	0	4.85	$3.8 \times 10^{-3}$
20	58.06	16.69	5.25	$3.02 \times 10^{-3}$
20	40.13	34.62	5.25	$1.88 \times 10^{-3}$

swollen by solvents containing the lithium salt. In Table 4, are shown some recent results of such materials.<sup>87</sup>

The electrolytes described above are well adapted in manufacturing Li-ion batteries. They can be used also for electrochromic devices as rocking chair batteries. However, these electrolytes are very hygroscopic due to the reactivity of lithium salts with water. It is therefore, necessary to protect the electrochemical devices from humidity. Actually it is an easy task for a small device like a battery, but a difficult one for a large system like a smart window. Therefore, there is an imperative requirement for hydrophobic electrolyte allowing the device building in an ambient atmosphere and in addition conferring a long lifetime.

Recently, this goal has been achieved by developing a hydrophobic salt, 1-ethyl-2-methyl-imidazolium trifluoromethane sulfonimide, which has been prepared by Grätzel *et al.*<sup>88</sup> This salt is a good solvent for lithium triflate. Then, this double salt can be mixed with a polymer like poly

(methyl methacrylate), which leads to an air stable film with a  $\text{Li}^+$  conductivity of  $10^{-3} \Omega^{-1} \text{cm}^{-1}$ ).<sup>89</sup> This new electrolyte, adapted to electrochromic devices or presumably to rocking chair batteries, is not electrochemically stable versus metallic lithium and can be only used in Li-ion batteries of low voltages ( $\sim 2$  V) (using for instance  $\text{Li}_x\text{TiO}_2$  as anode and  $\text{LiMn}_2\text{O}_4$  as cathode).

**Electrochromic Materials.** The most popular electrochromic material is  $\text{WO}_3$ , which is colorless when stoichiometric. It turns into blue when ions ( $\text{H}^+$ ,  $\text{Li}^+$ , etc.) are inserted in its lattice. This oxide is generally shaped in transparent film by sputtering. We have recently proposed a new process using IOH-cc and dip coating.<sup>90-92</sup>

Poly(acrylic acid) (PAA) has a good adhesion on ITO films used as transparent electrodes in electrochromic devices. In addition, PAA reacts with a solution of  $\text{WO}_3$  dissolved in ammonia leading to an IOH-cc containing  $\text{W}^{5+}$ . Films are prepared by dip or spin coating, where we can describe the formation of stable PAA/ $\text{WO}_3$  composite film by the chemical acid-base interaction (Fig. 10) After the electrochemical formatting in HCl solution, the films (Fig. 11) show a reversible and deep electrochromism with a good colour homogeneity. This process can be used to manufacture cheaply large area smart windows.<sup>93</sup>

**Sensor Membranes.** The development of chemical detectors for the gaseous or liquid pollutants in environmental or industrial applications is currently a topic of growing interest.<sup>94</sup> Zeolites might

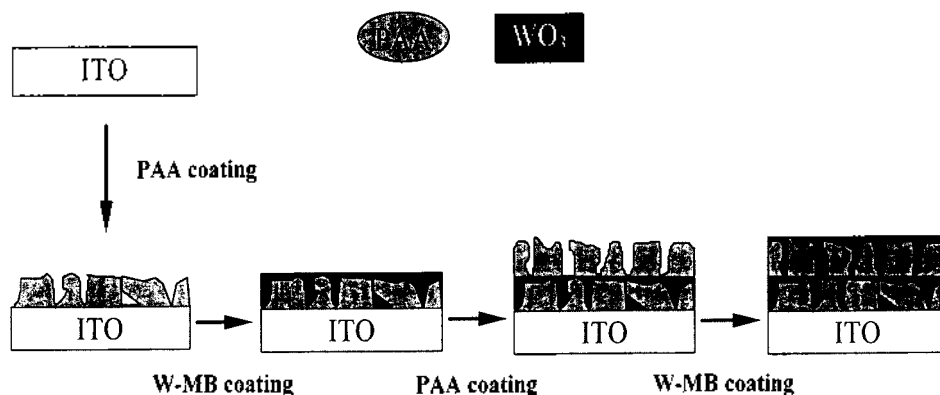


Fig. 10. Schematic diagram for the sol-gel coating of PAA/ $\text{WO}_3$  film.

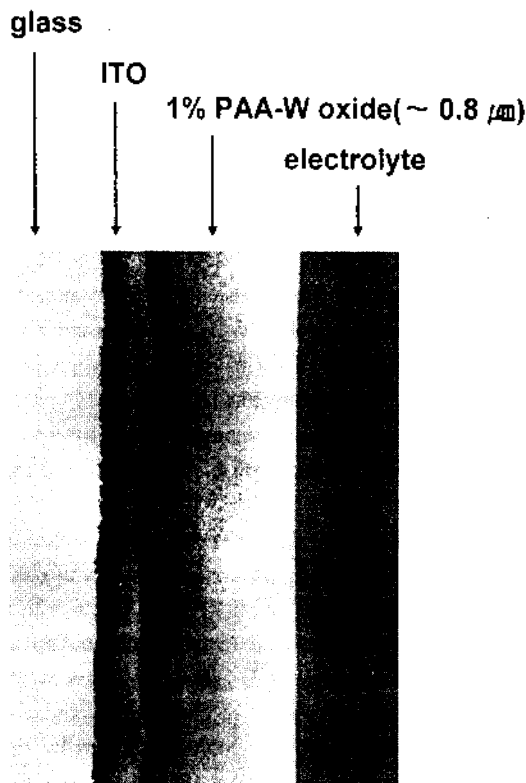


Fig. 11. Electrochromic films prepared by dip coating.

be the most familiar compounds, which are size- or charge-selective for specific chemicals. But, in a more simple and systematic way, highly porous media can be constructed with various pore sizes up to 20 Å. They are accomplished by the intercalation of mixed or pure oxide sols into the layered aluminosilicates through the post-intercalation of organic templates (*Fig. 12*).<sup>95</sup> In the case of electrochemical sensors, the modern trend is to replace the classical ion specific electrodes (like glass electrodes for pH measurement) by electronic devices such as ISFETs (Ion Sensitive Field Effect Transistor), which have been proposed by Bergveld.<sup>96</sup> Basically, the ISFET is a metal oxide field effect transistor where the gate is replaced by an ion sensitive solid state electrode inducing a current modulation in the channel of the FET (*Fig. 13*). IOHs are exceptionally suitable for manufacturing ISFET membranes. Indeed, it is easy to fix the activity of the species to analyse by doping the IOH with proper ion or molecule. In addition, the FET coating by a gel can be obtained by a simple painting.

Thousand references can be found on this subject. Thus, in this short review we will give only

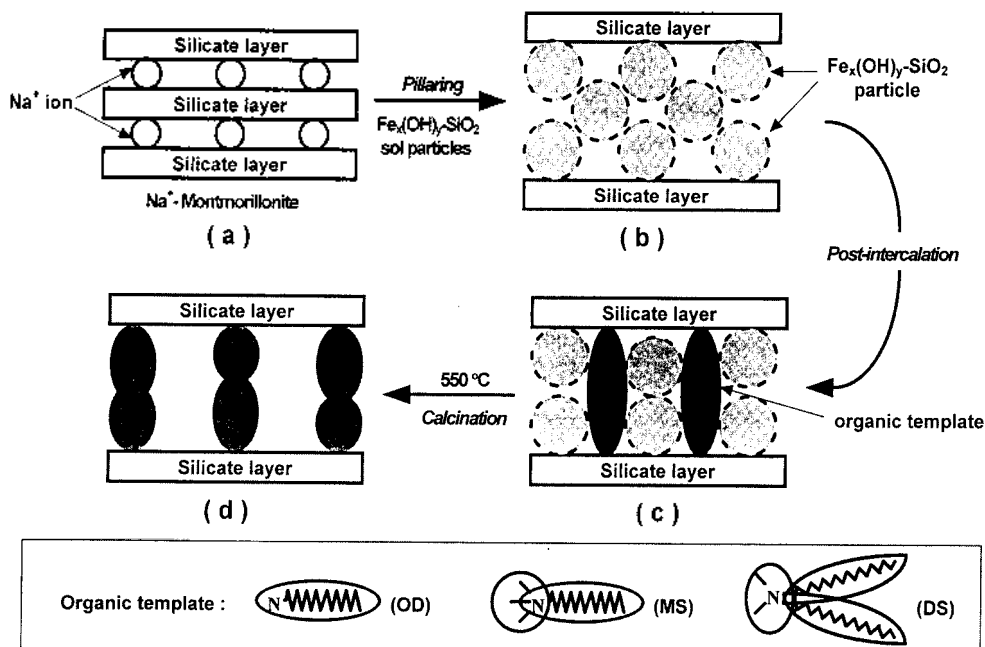


Fig. 12. Schematic model for the formation of mesoporous silica iron sol pillared clays.

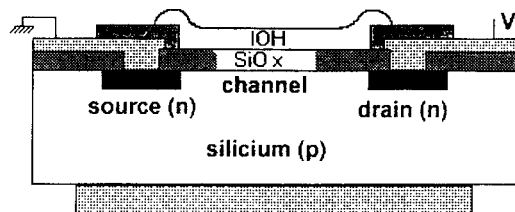


Fig. 13. Scheme of a Ion Sensitive Field Effect Transistor.

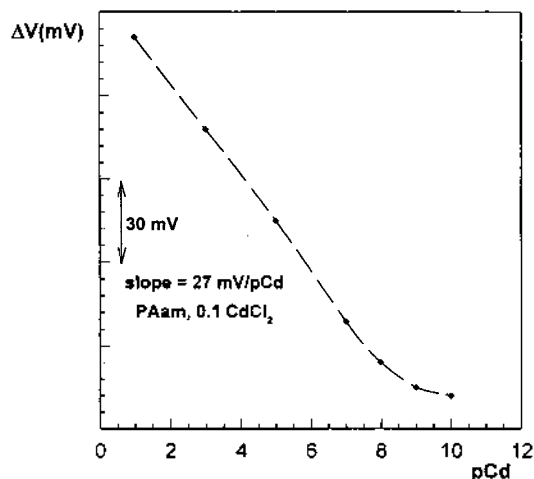


Fig. 14. Voltage versus pCd of PAam, 0.1 CdCl<sub>2</sub> membrane.

one example dealing with the detection of Cd<sup>2+</sup> pollutant in solution.<sup>97</sup> The previously cited IOH-cc, poly(acryl amide)-xCdCl<sub>2</sub> can be used for such purpose (Fig. 14). A Nernst law is observed for a double charged ion (27 mV/pCd). The detection limit is very low (~1 ppb).

#### From Hybrid to Bio-hybrids (BIOH)

Bio-molecules or macromolecules (nucleic acids, proteins, ...) are chemically very close to polymers. They contain organic groups reacting with inorganic ions according to either Brønsted or Lewis acid-base reactions. Some inorganic ions are necessary for the life (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>), but some others are very toxic (Li<sup>+</sup>, Rb<sup>+</sup>, Be<sup>+</sup>, Sr<sup>2+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup>, ...). As a consequence, inorganic complexes are widely studied in biochemistry.

In the case of DNA, inorganic complexes are studied either for their toxicity or, on the contrary, as drugs to cure various diseases. For example, the

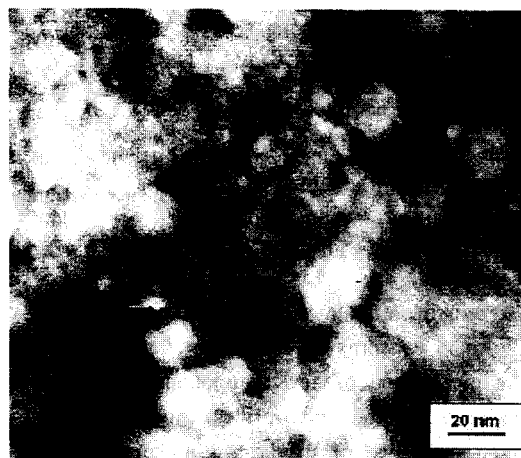


Fig. 15. CdS nanoparticles in a herring DNA matrix.

chromium with higher oxidation states (4<sup>+</sup>, 6<sup>+</sup>) is known to be highly carcinogen; It has been shown that these ions initiate DNA cleavage.<sup>98</sup> As a counterexample, one can mention the antitumour activity of ruthenium complexes.<sup>99</sup> The general philosophy of these researches is to know to what reactive sites, phosphate groups, sugar moiety or bases, the inorganic cation is fixed.<sup>100</sup>

In the field of hybrids, another category of researches concern the encapsulation of biomolecules in inorganic matrix. One can notice the incorporation of antibodies<sup>101</sup> or proteins<sup>102</sup> in sol-gel matrices. Two-dimensional nanocomposites of aminoacids in zirconium phosphate<sup>103</sup> and gold nanoparticles in oligonucleotides, have been reported.<sup>104,105</sup> Recently, Coffey *et al.* announced the formation of semiconducting CdS nanoparticles connected to plasmid DNA.<sup>106</sup> We obtain an analogous result on herring DNA. This macromolecule gives a solid complex with cadmium iodide according to the ratio phosphorus/cadmium ≈ 1. In this hybrid, soaked during few seconds in a water solution of diluted ammonium sulphide, 20-30 Å CdS nanoparticles are formed (Fig. 15).<sup>107</sup> And, at present, we have achieved positive results that some base-monophosphates are intercalated into cationic layered double hydroxides (Fig. 16).<sup>108</sup> Therefore, it is possible to prepare not only LDH-plasmid DNA composites but also RNA ones.



Fig. 16. Schematic diagram for DNA encapsulated with LDH.

## CONCLUSION

From the middle of the present century, one of the main concerns of solid state chemists has been the preparation of new compounds. Due to these endeavors, at the end of the century, there is an over-abundance of materials compared to the industrial needs. Consequently, a new deal arises epitomized by the words «smart materials». In fact materials by themselves are not «smart» but they can become interactive when associated with other materials in a system. Consequently the attention for materials is twisting in the direction of systems.

The hybrids described in this survey are particularly well adapted to this new deal. Indeed, due to their double inorganic (or biological) and organic nature, they could have very flexible and adaptable properties. Moreover, easy to be shaped in any conformation, and particularly as films, they are adapted as parts of various devices such as electrochromic devices, batteries, sensors and more generally to MEDs (Molecular Electronic devices).

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