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Journal Name

Electro-chemo-biomimetics from Conducting Polymers: Fundamentals, Materials, Properties and Devices

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Conjugated conducting polymers, intrinsic conducting polymers or conducting polymers are complex and mixed materials, which electroactive fraction follows reversible oxidation/reduction reactions giving reversible volume variations to lodge, or expel, charge balance counterions and osmotic balance solvent molecules. The material content (reactive macromolecules, ions and water) mimics the intracellular matrix (ICM) dense gel of living cells. Here the electropolymerization mechanism is revised highlighting the presence of parallel reactions resulting in electroactive and non-electroactive fractions of the final material. Conducting polymers are classified into nine different material families. Each of those families uses to follow a prevalent reaction-driven exchange of anions or cations during oxidation/reduction (p-doping/p-dedoping or n-doping/n-dedoping). Polyaniline families also follow reaction-driven exchange of protons. The polymer/counterion composition changes for several orders of magnitude in a reversible way with the reversible reaction. The value of each of the different composition-dependent properties of the material also shifts in a reversible way driven by the reaction. Each property mimics another changing in functional biological organs. A family of biomimetic devices is being developed based on each biomimetic property. Those electrochemical devices work driven by reactions of the constitutive material, as biological organs do. The simultaneous variation of several composition-dependent properties during reaction announces an unparalleled technological world of multifunctional devices: several tools working simultaneously in one device. Either, properties and devices are driven by electrochemical reactions: they are Faradaic devices and must be characterized by using electrochemical cells and electro-chemical methodologies.

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Summary

Introduction: The beginning

At the end of the 70ths from the last century Professors MacDiarmic, Heeger and Shirakawa^{1,2} realized that a polyacetylene film could change its electronic conductivity by over 7 orders of magnitude (from insulator to 10^3 S cm^{-1}) under doping/de-doping, according with the physical terminology, or under reversible oxidation/reduction, chemical terminology. The discovery was acknowledged with the Nobel price of chemistry 2000. This was the beginning of the explosion of a new field of research, even if some of the components had been discovered years before.³⁻⁵ Since then the exponential increase of the number of papers has been giving numerous reviews, books and handbooks.⁶⁻¹⁵

Materials

Despite the bibliographic explosion few efforts have been done to attempt a classification of this material's forest. Up to 9 different material families have been proposed,^{8,16,17} each constituted by hundreds of different materials, of which only a very low percentage have been synthesized at present. For clarification we will present here the different polymeric materials used for the construction and control of electrochemical devices (electrodes or electrolytes): electronic and ionic conducting polymers, redox polymers, pure ionic conducting polymeric electrolytes and polyelectrolytes (commodity or biological).

Basic conducting polymers.

Following their discovery, scientists realized that a lot of heterocycles such as thiophene, pyrrole, furan, aniline, carbazole,... (Figure 1a, every empty corner is a C-H group) could be polymerized giving polythiophene, polypyrrole, polyfuran, polyaniline, polycarbazole... (Figure 1b). Following calculations from quantum mechanics the theoretical electronic conductivity of those molecules could be shifted, in average, by oxidation/reduction from 10^{-9} to 10^3 S cm^{-1} . In fact

by structural reasons getting lower experimental conductivities than $10^{-4} \text{ S cm}^{-1}$ is a difficult task for films thicker than $1 \mu\text{m}$.¹⁸

Monomeric and polymeric derivatives.

After formation of ideal lineal chains of conducting polymers (ahead CP) (Figure 1b) each monomeric constituent still contains two or more C-H groups. Coming back to the monomeric units, one or two of those H atoms can be substituted by other chemical groups, figure 2. The substituent can be selected to change, under tailored design, some of the properties (electronic or ionic conductivity, optical, mechanical, stored charges, stored ions, sensing properties, band-gap, and so on) of the final polymer. Substituted monomers originate two main families of CPs:

Substituted conducting polymers, where at least one of those H is substituted by an organic group bearing a characteristic (electron donor, electron acceptor, chromogenic, flexible, ...) selected to change one of the properties of the final polymer, like its bandgap.¹⁹⁻²³

Self-doped conducting polymers or conjugated polyelectrolytes, where the substituent is an ionic (anion/cation) organic component. One of the ions is covalently bonded to the monomeric unit; the second ion will be exchanged with the electrolyte during doping/de-doping processes.²⁴⁻²⁷

The only limitation to design new substituted monomers in order to get tailored polymeric properties is our knowledge related to basic organic chemistry and steric limitations: too large substituents only allow, by steric hindrance, the subsequent formation of oligomers even dimers. This possibility has been exploited to get soluble conducting oligomers.^{24,28-30}

Copolymers. Two or three basic, or substituted, monomers can be linked to form a dimer or a trimer, which can be used as a basic monomer to synthesize a copolymer. On this way soluble and electrochemically solubilized/electrodeposited polymers had been synthesized.³¹⁻³⁶

Conducting organic blends and conducting polymer-inorganic hybrids.

During synthesis (see below) conducting polymers are generated as oxidized materials requiring a counterion for charge balance. When a large organic or inorganic counterion, having specific mechanical, optical, electrical, electrocatalytic or magnetic properties is used, it remains entangled with, or trapped by, the polymeric chains forming a conducting polymeric compound. Two basic families are being developed:

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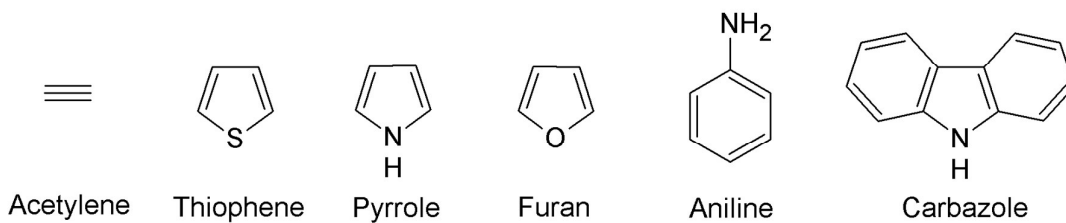
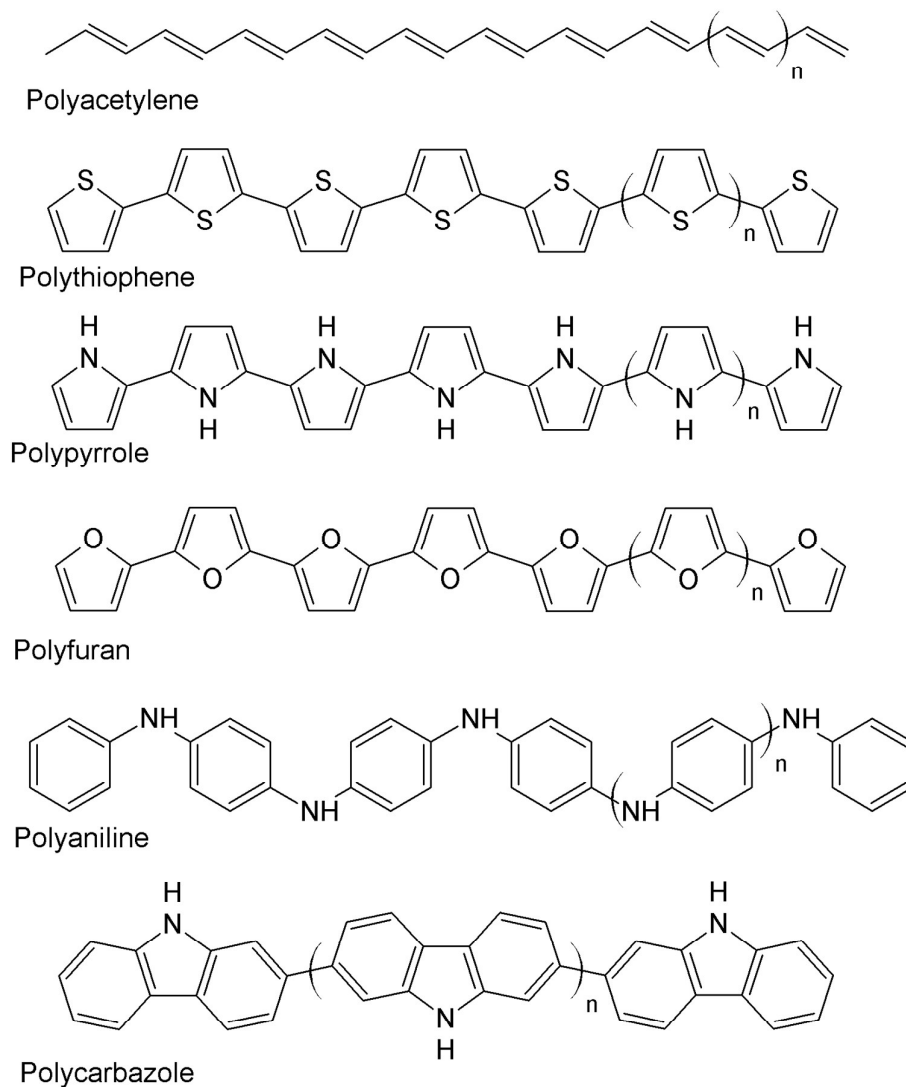
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Fig. 1 Some monomers (a) and their conducting polymers (b).

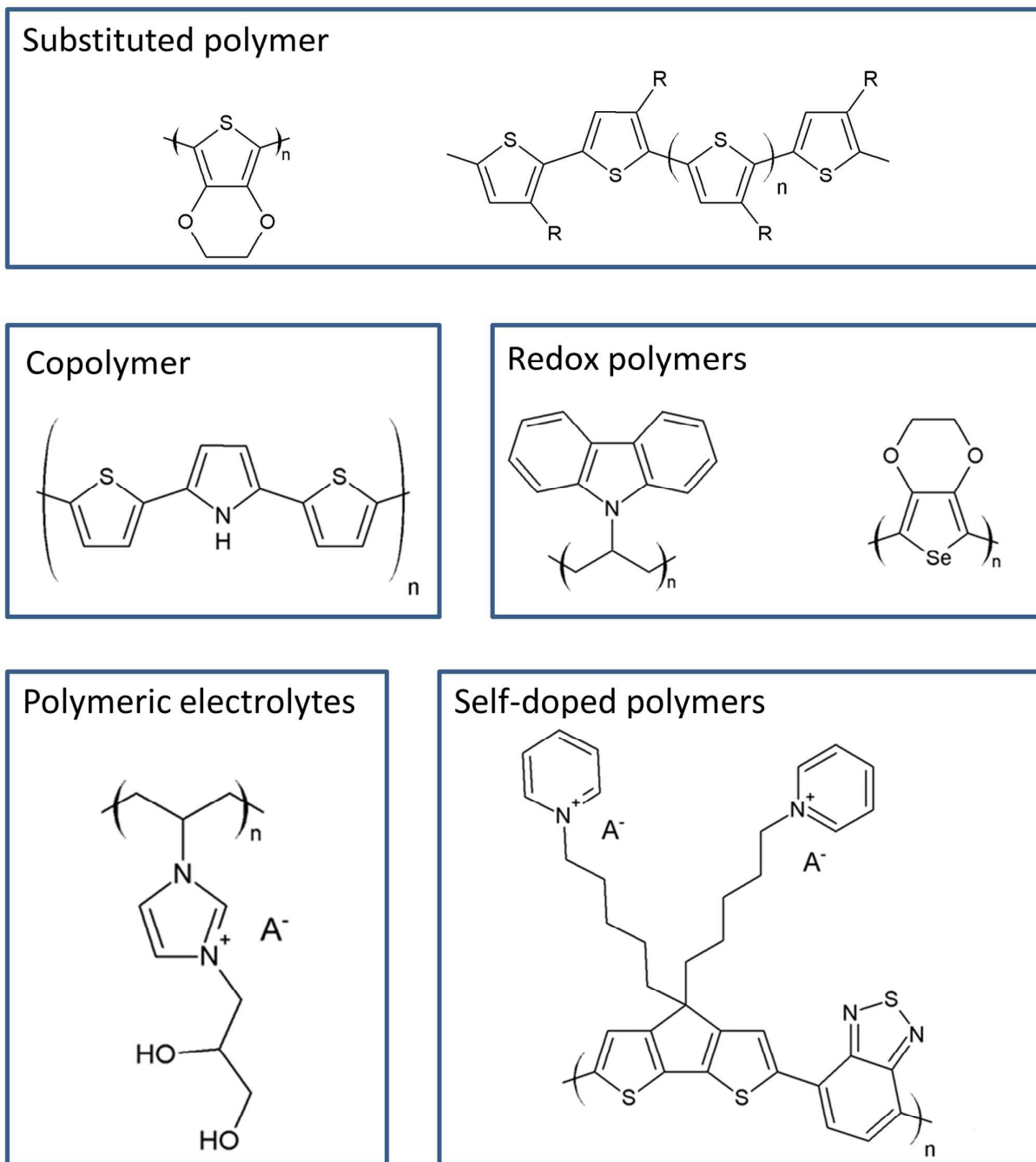


Fig. 2 Examples of substituted polymer, copolymer, redox polymers and polymeric electrolytes.

Organic blends: polyelectrolytes,^{37,38} large organic acids or large organic salts, as surfactant amphiphiles³⁹ and other organic molecules like alcohols or sugars⁴⁰ used during the synthesis of the CP are incorporated to the final material forming smooth and flexible films of an organic blend.

Inorganic hybrids: electroactive, magnetic active or electrocatalytic poly-oxo-metallates^{41,42} or double layer hydroxides,⁴³ are trapped during the CP's synthesis to form conducting polymer-inorganic hybrid materials.

Organic and carbon based electroactive composites.

The electrogeneration of a conducting polymer in presence of carbon based structures like carbon nanotubes,^{44,45} fullerenes,^{46,47} graphenes,⁴⁸ graphite or carbon powder⁴⁹ gives composite materials of the CP, which two components are electroactive.

Other composites using conducting polymers.

From solutions of CPs a mixed material can be formed with small (microscopic, nanoscopic or clusters) pieces of any other material as metal, plastic, gel, vesicles. Any composite is expected to keep the same electrical and electrochemical properties of the constituted conducting polymer host, plus some of the properties of the lodged material.^{36,50-54}

Salts of conducting polymer.

Any component of the above eight families of conducting polymers can be considered as a metal of the periodic table of elements. Every metal can form hundreds of metal compounds: oxides, halides, sulphides, nitrates, phosphates, organic complexes, and so on. From every conducting polymer hundreds of polymeric compounds (different conducting polymers), similar to the metal salts, can be formed. The easiest procedure is an electrochemical substitution of the balancing counterions in an electrolyte having the new counterion through the basic electro-chemical reactions described in the section entitled 'Reversible doping/de-doping, or oxidation/reduction, of CPs under electrochemical control'.

Redox polymers

The polymer chain is an electronic insulator but, some lateral redox groups can be reversibly oxidized and reduced opening the way for electronic tunnel jump between them.^{55,56} They cannot be considered as intrinsic conducting polymers due to the absence of conjugated polaronic structures along the chain.

Ionic conducting membranes or polymeric electrolytes

Polymer insulators bearing high dipolar moments can solve large amount of ionic liquids (IL) and, when molten, large amount of salts promoting their dissociation. Solid films obtained from those solutions work, above its t_g (glass transition temperature), in electric fields as solid electrolytes with relatively high ionic conductivity and null electronic conductivity.⁵⁷ They constitute the supporting polymeric film electrolyte for the construction of full polymeric electrochemical devices (artificial muscles, smart windows, batteries and so on), where the intrinsic conducting polymer electrode is the electroactive material origin of the actuation.

Polyelectrolytes

Polyelectrolytes are polymer chains (electronic insulators) with lateral ionic substituents. Artificial polyelectrolytes were developed for car electro-painting technologies.^{58,59} Gels with solvated salts also are named polyelectrolytes.⁶⁰ Most of the biological polymers which reactions originate living functions

are polyelectrolytes.^{61,62} Some polyelectrolyte films also can act as anionic or cationic conducting membranes being electronic insulators. Recently polymeric ionic liquids (PIL), or liquid polyelectrolytes⁶³ are focusing a great interest.

Taking into account that any conducting polymer bears charges on chains (polarons or bipolarons) and mobile balancing ions between chains could be also considered as poly-conjugated (electronic conducting) polyelectrolytes.

Electrochemical synthesis of conducting polymers

Polymerization and electropolymerization are fast processes through complex mechanisms or parallel reactions giving mixed materials: electroactive and non-electroactive fractions.^{8,9,16,17,64} Scientists and engineers are looking for CPs working at very low voltages, with high electroactivity. Thus, for actuators or artificial muscles (see below) they are looking for large amplitude of the described movements for low charge and energy consumption getting high efficiencies to produce mechanical energy per unit of consumed electrical energy. Those conditions only can be attained if, during synthesis, those parallel processes giving non-electroactive material (increasing the resistance of the final material) are minimized. Those researchers controlling the synthesis mechanism will have great advantages to develop improved materials and products.

The synthesis of CPs requires a solution including the monomer (M) and a solvated salt (anions, A^- and cations, C^+), and an initiation step.

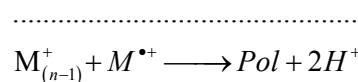
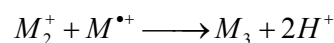
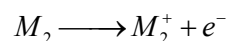
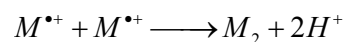
Mechanism.

Several of the following steps coexist during the polymerization mechanism:

Initiation. From every monomeric unit the polymerization is initiated by physical (light, heat, mechanical,...), chemical or electrochemical generation of radical-cations:



Polymerization. By polycondensation of radical cations followed of a new initiation step.



(2)

Those two steps constitute the generally accepted polymerization and electropolymerization mechanism.

This basic mechanism is unable to explain why the synthesis of the same conducting polymer (as polythiophene) under similar

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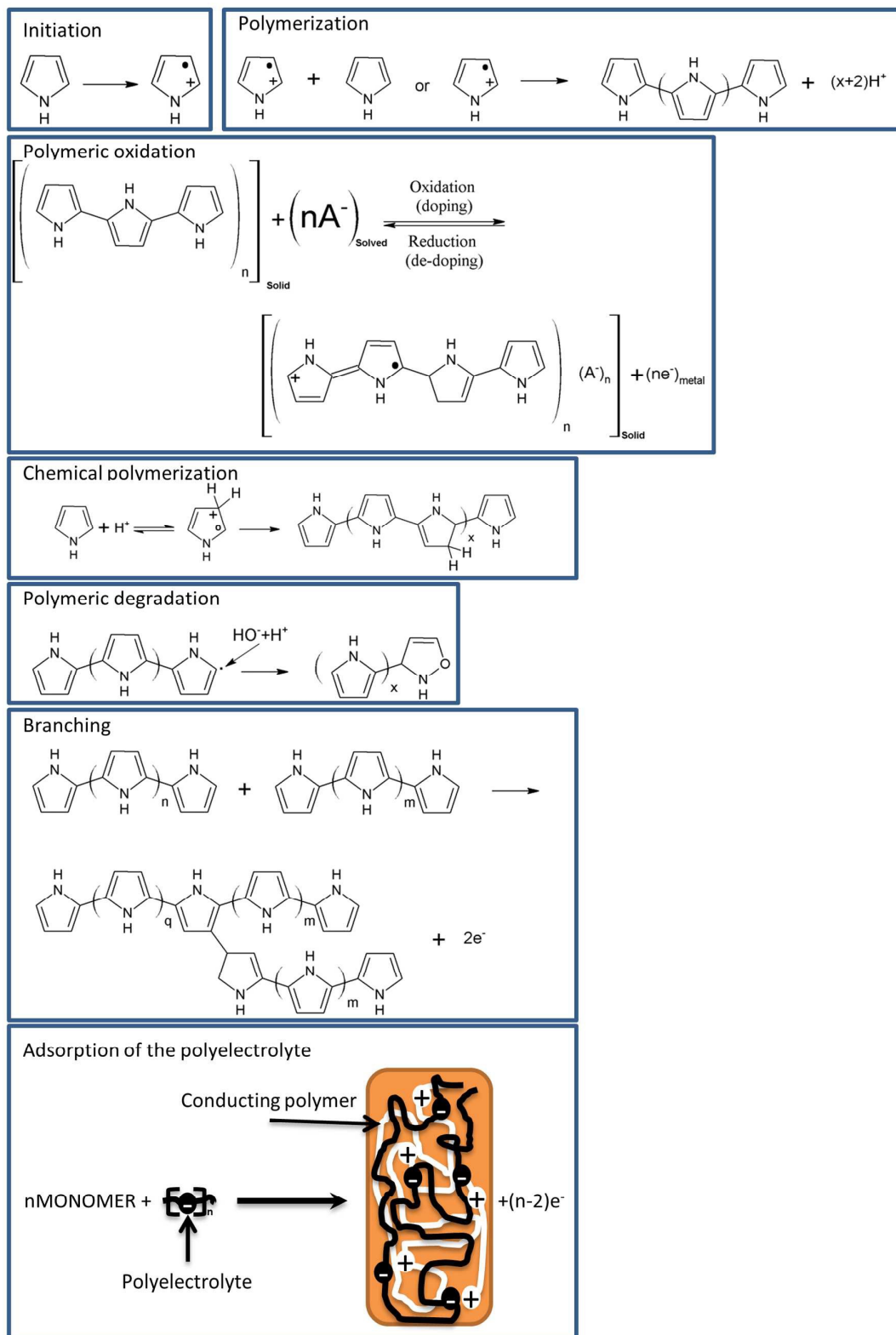
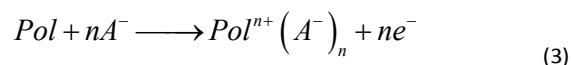


Fig. 3 Electropolymerization steps: several steps coexisting during the synthesis of conducting polymers.

conditions in different laboratories gives different physical (conductivities spread through 6 orders of magnitude), chemical and electrochemical properties of the generated CP.

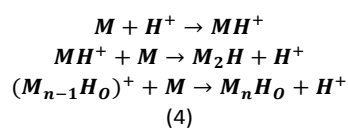
Polymeric oxidation. The oxidation potential of the generated polymer chains (Pol) is lower than that of the original monomer, thus the generated chain is immediately oxidized to generate, with balancing counterions (A^-), a polymeric salt $[Pol^{n+}(A^-)_n]$ through the reaction:



Branching. Some of the remaining H on the monomeric non-substituted unit of a polymeric chain can be removed during polymerization to initiate the formation of a new lateral chain (Figure 3). The breaking conjugation along the chain decreases the material conductivity and electroactivity (charge stored per unit of weight): this is a degradation reaction in the sense that it promotes a change of the polymeric properties.

Cross-linking. When a growing lateral chain meets the polaron of a neighbour chain a cross-linking process takes place diminishing the solubility of the polymer material (Figure 3). The breaking conjugation along the three connected branches also decreases the material conductivity and electroactivity: this is a degradation reaction.

Parallel chemical polymerization. When the polymerization occurs in absence of protophilic species those protons generated during the polymerization process (reactions 2) can attack the monomer (changing from sp^2 to sp^3 the hybridization of one of the C from the monomer) to initiate the chemical polymerization of a protonated (low conjugation) polymer:



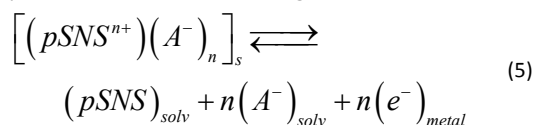
When those protonated monomeric or polymeric units are incorporated into the polymer (Figure 3) the conjugation loss of the protonated polymer gives high resistive chains.⁶⁵⁻⁶⁸ The proton's concentration during electropolymerization processes is very high around the electrode originating a cloud of brown polymer dropping towards the solution. The growing conducting polymer film traps a fraction of this non-conjugated polymer generated around the electrode giving a rising fraction of non-electroactive material: this is a mixed material with decreasing conductivity and electroactivity for rising content of the protonated polymer.

Adsorption of macroions. Macroions are adsorbed on surfaces allowing the formation of multilayers.^{37,69-71} When the polymerization (or electropolymerization) occurs in presence of large molecules or ions (organic salts, surfactants, polyelectrolytes, ionic liquids) the concomitant ion couples are

adsorbed on the surface of the growing material. The salt composition in the final material is higher than that required for charge balance (Figure 3) and the film specific electroactivity (charge stored per unit of weight) decreases. This step increases the composition of non-electroactive material in the final synthesised CP increasing its electrical and chemical resistance and de-creasing its electroactivity.⁷²⁻⁷⁶

Degradation. When the chemical or electrochemical ambient during the polymerization is strong enough (high overpotential with water-or residual water- electrolysis) the radical-cations (polarons) of the oxidized polymer can be attacked by an organic or aqueous radical forming a new sp^3 chemical group, losing the conjugation of the involved C atom from the chain (Figure 3) and originating the progressive degradation (overoxidation) of the polymer electrical and electro-chemical properties.⁷⁷⁻⁸⁰

Electrodissolution. When the polymerization process originates linear oligomeric compounds (salts) and the solubility of the oxidized compound is high, a solution is attained. When the solubility of the oxidized and reduced material in the same electrolyte is very different the polymer can be reversibly solved/deposited by current flow,^{32,35,81,82} the amount of solubilized/deposited material being a linear function (faradaic process) of the involved charge.



where pSNS is poly(2,5-di-(-2-thienyl)-pyrrole) the sub-indexes mean: s, solid; sol, solvated in solution, and metal electrode. Electrochemical solubilisation and electro-deposition are parallel processes to those taking place using metals during plating, electromachining, electropolishing, electrodissolution and so on. Taking into account the plethora of technological applications from the reverse electrodisolution/electrodeposition of metals, it surprises the null technological interest for similar processes using conducting polymers.

Chemical initiation.

Different oxidants are used for the chemical polymerization initiation of monomeric solutions: $FeCl_3$, $CuCl_2$, I_2 , Br_2 , Cl_2 , $K_2S_2O_8$, 2,3-dichloro-5,6-dicyano-p-benzoquinone, $FeOCl$, $K_3Fe(CN)_6$, $FeCl_3 \cdot 6H_2O$, $Fe(SO_4)_3 \cdot 5H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Fe(ClO_4)_3 \cdot 9H_2O$, $FeBr_3$, $CuCl_2 \cdot 2H_2O$, $CuBr_2$, $FeCl_3$, $Fe(BF_4)_4$, $Na_3(PO_4 \cdot 12WO_3)$, among others, have been used from the very beginning.⁸³⁻⁸⁵ The generated salt of the conducting polymer (oxidized) precipitates as a black powder, which can be rinsed, dried and pressed.

The procedure also can be used to produce interpenetrated polymer network films. When a film, wire or textile of a dense membrane, commodity polymer, natural fibre, wood or other material is present in the monomeric solution before the initiator addition, the polymerization is also initiated from the

monomeric units absorbed just below the material surface. A coating conducting polymer film is formed on the used material giving an interpenetrated (super-adhesion) polymeric network with the substrate. In parallel most of the polymer is formed in solution as a powder. On this way trilayers CP/membrane/CP for different application (including artificial muscles) can be attained.

Soluble conducting polymers.

Under the above conditions most of the generated powders or films of conducting polymers result branched and crosslinked: most of the material is insoluble in any solvent and must be used as powder, pressed pills or films. By softening the polymerization conditions, or by using substituted monomers or end-capped monomers, a great control of the polymerization is achieved getting, even, monodisperse oligomeric solutions. Those solutions can be used to produce electrochemical devices by using cheap printing, dipping or spin-coating technologies.^{24,86-90}

Electrochemical synthesis summary.

Summarizing, the synthesis of conducting polymers is a fast process through a complex mechanism including, at least, initiation, polymerization and polymer oxidation steps. The parallel presence of other steps as branching, crosslinking, polymer degradation, absorption of large molecules or ions, or chemical polymerization by protonation originates a mixed material constituted by electroactive and non-electroactive fractions. Thus, during the synthesis of polythiophene from acetonitrile in different laboratories the water content changes from 0 to 2% as a function of the relative humidity. The required high anodic potentials for the monomer oxidation/polymerization promote the simultaneous water discharge with partial degradation of the electrogenerated polymer⁹¹. The conductivity of the attained polythiophene changed as a function of working laboratory conditions.

The reaction rate of each of the above parallel reactions can be controlled, or eliminated, allowing the obtention of tailored materials for specific applications. Thus, a low initiation rate (low oxidant initiator concentration, low temperature or low anodic overpotential) can diminish either polymeric branching, cross-linking and degradation rates. The parallel proton initiated chemical polymerization of passive chains in aprotic media can be avoided by adding a low concentration of a protophilic compound, as water, until attaining a concentration compromise: above 1-2 % water contents promote rising degradation rates by water electrolysis.

Adding small amounts of large ions or molecules allow the generation of most uniform films or structures: they are adsorbed by the growing nuclei forcing a uniform nucleation and growth (as they have been doing for one century in parallel electroplating technologies).

A good control of the polymer synthesis is a key point to improve the efficiency of any electrochemical device based on conducting polymers. Only the electroactive fraction of the final material drives the device's actuation. Rising degradation, crosslinking, chemical polymerization and/or absorption of macroions (ahead that required for charge balance) rates

during the polymerization reaction give less electroactive materials. That means that the construction of the best electrochemical device based on conducting polymers is initiated by a good design of the CP synthesis conditions.

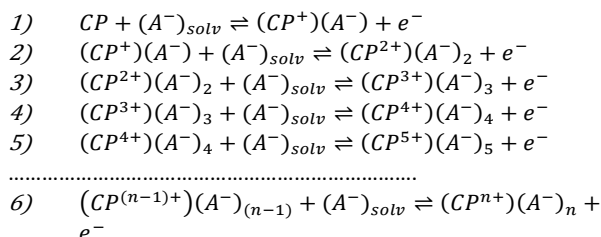
Reversible doping/de-doping, or oxidation/reduction, of CPs under electrochemical control.

After synthesized the CP film is used to manufacture electrochemical devices. Each chain of any conducting polymer electrode follows oxidation/reduction (doping/de-doping) reactions requiring the exchange of ions and solvent between the film and the electrolyte for charge and osmotic balance. The Faraday's law gives through the consumed charge (Q) the number of ex-changed ions (n).

$$n = \frac{Q}{ze^-} \quad (6)$$

where e^- ($1,602 \cdot 10^{-19}$ C) is the electron charge and z the ion charge.

Each electroactive polymeric chain of the CP film has a first, second, third,..., nth ionization potential for the extraction of the first, second, third,..., nth electron, thus it moves from the neutral chain through n , theoretically, consecutive oxidation states. Reaction 3 can be rewritten as:⁹²



(7)

Each of those n steps constitutes a stable oxidation equilibrium state of the material with an equilibrium potential described by the Nernst equation being $E_1 < E_2 < E_3 < \dots < E_n$ (giving nernstian sensor). By control of the oxidation charge, or of the oxidation potential, we can reversibly move through each of the oxidation states, thus through a CP:anion composition ratio going from 1:0 to 1:n, covering the n intermediate states.

In an ideal monodisperse (all the chains have the same length) film of any CP the first chain moves to the next oxidation state (1:i) only when all the chains have completed the previous oxidation state (1:i-1). The chemical potential at any intermediate time is constant (the composition is uniform) across the film, changing along the oxidation time.^{93,94}

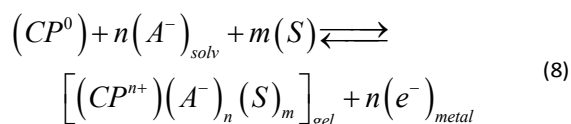
The n consecutive steps from reaction 6 can be rewritten for the polymeric reduction (by injection of electrons) from the neutral state, n -doping. The composition ration (CP/ion) of any CP electrode can be sifted, under control (reactions 7) of the consumed electrons (charge) through several orders of

magnitude (giant non-stoichiometry) due to the faradaic exchange of the balancing ion.

In presence of a liquid electrolyte the entrance of those ions with parallel increase of charges on chains changes the film ionic concentration forcing the physical entrance of solvent for osmotic (quantified by the Van't Hoff law) balance.

Oxidation (p-doping) with exchange of anions.

Consecutive reactions (7) are summarized in the literature, including solvent exchange required for osmotic balance, as:^{95,96}

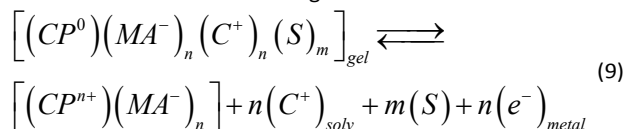


where CP^0 represents neutral conducting polymer chains, CP^{n+} represents oxidized conducting polymer chains and S represents solvent molecules exchanged to keep the osmotic balance inside the formed dense gel (indicated by subindex gel).

The polymeric chains store consecutive positive charges (p-doping); anions and solvent penetrate from the solution for charge and osmotic balance forming a dense gel. In order to lodge/expel so huge amount of counterions and solvent the polymer film swells/shrinks, respectively, under oxidation/reduction control. Basic CPs, substituted CPs and copolymers use to follow this reaction during oxidation/reduction from the neutral state.

Oxidation (p-doping) with exchange of cations.

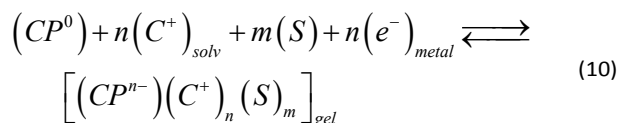
The macroanions of the polymeric blends remain trapped in the material during oxidation/reduction forcing the exchange of cations and solvent for charge and osmotic balance.^{8,92}



The electrode swells by reduction and shrinks during oxidation. Self-doped CPs and polymeric blends of CPs use to follow this reaction.

Reduction (n-doping) with exchange of cations.

The electronegativity (energy required to accept electrons) of some conducting polymers, as thiophene and thiophene derivatives, is low enough to allow the polymer reduction inside the potential window of different organic electrolytes. The polymer stores consecutive electrons (n-doping) exchanging cations and solvent for charge and osmotic balance. The reaction can be summarized as:^{17,22}

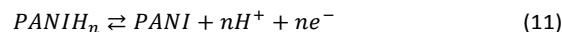


The polymeric electrode expands during reduction by entrance of cations and solvent and shrinks during oxidation.

Oxidation/reduction with exchange of protons from polyaniline derivatives.

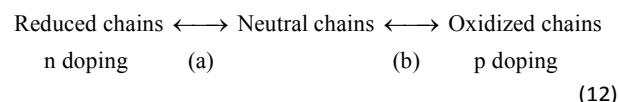
Polyaniline (PANI) and the family of polyaniline derivatives before the exchange of anions (reaction 8) experience a

reversible exchange of protons by oxidation/reduction in aqueous solutions of different salts:⁹⁷⁻⁹⁹



Electrochemical bandgap

Some CPs can be oxidized (p-doped) or reduced (n-doped) from the neutral state:



When they are characterized by cyclic voltammetry the energy difference between the beginning of the oxidation (rising anodic current) and that of the polymer reduction (rising cathodic currents) is the electrochemical bandgap energy of the CP.^{22,100} This energy can be tailored by organic chemists using suitable electron donor or electron acceptor groups as substituent of H atoms in the basic monomer (Section entitled 'Substituted conducting polymers').

Consecutive oxidation or reduction reactions.

The reaction-driven ionic exchanges are identified by XPS or other analytical methodologies for different oxidation states of the conducting polymer.¹⁰¹⁻¹¹⁰ Bending artificial muscles together coulombometric and dynamo-voltammetric (angle-potential) responses result very efficient to follow parallel volume variations and structural changes. They allow the separation of irreversible reactions,¹¹¹⁻¹¹³ solvent exchange¹¹⁴⁻¹¹⁶ and ionic exchanges.^{18,117} Some conducting polymers (in particular blends of CPs with intermediate shape organic anions) can move from reaction-driven exchange of cations at low potentials to anion driven exchange at high potentials.^{118,119} When the solvent is changed, for the same salt the system moves from reaction-driven exchange of cations to reaction-driven exchange of anions.^{120,121} Those are excellent material models for a quantitative investigation of the intermolecular forces variation inside the reactive dense gel getting models that can be translated to similar processes in living cells.⁹⁶

Electrochemical transformation between polymeric compounds.

The chemical nature (polymeric salt) of any CP can be changed by using reactions 8 to 10 to exchange the charge balance anion, or cation, giving a new conducting polymer (a new salt). The original film is translated into a solution of the new counterion. After several reduction/oxidation (p-doping) or oxidation/reduction (n-doping) cycles the new conducting polymer is attained.

At the moment steric constrains avoid the reversible exchange of large anions, as polyelectrolytes, large neurotransmitters, large ions of pharmacological interest or large fertilizer salts by substitution of a small anion.^{95,122} The electrogenerated free volume inside the material is not large enough (structural limitations), at the moment, to allow the reversible exchange of macromolecular ions.¹¹³

Composition dependent conductivity and based technological developments

Consecutive reactions (7) generate consecutive conjugated radical cations (polarons) uniformly distributed along the polymeric chain. The progressive increase of the conjugated fractions gives rising electronic conductivities through n consecutive electrochemical equilibrium states. The conductivity can be reversibly tuned by the concentration of conjugated states defined from Eq. 6.

The availability of soluble oligomers and the theoretical possibility to tune the final electronic conductivity of the material from 10^7 to 10^3 S cm⁻¹ have generated great expectancies to re-construct either electronic,^{123–128} microelectronic and optoelectronic^{129–131} components on any support (rigid, flexible, film, textile, ...) getting transparent components and using cheap printing or dipping technologies. In parallel those oligomers could be used as molecular wires to build and connect molecular electronic components. Most of the researchers working with CP are there involved and a lot of products are arriving to the markets. A solid theoretical background, developed during the XX century for inorganic semiconductors, supports those technological developments.

Intracellular matrix (ICM) material model for living cells: Biomimetic Properties.

In aqueous solutions reactions 8–10 provide dense reactive gels constituted by reactive macromolecules, ions and water. They mimic, in its simplest expression, the ICM of living cell: similar reactions from the organ cells involving proteins, enzymes or nucleic acids originate life and life functions.⁹⁶

Composition dependent (chemical) biomimetic properties.

The CP/counterion composition shifts, through reactions 8–10, in a reversible way under control of the involved charge. The magnitude of any composition-dependent property of the dense gel also must change in a reversible way.⁹ With the ionic content they change: volume^{102,132–140}, colour^{38,141,141–144}, stored charge^{145–148}, stored ions,⁹⁵ liberated ions,^{95,149–151} porosity, transversal ionic diffusion,^{95,152–157} electrode potential, consumed energy, conformational energies, molecular interactions, surface properties as wettability or energetic conformational states of the material.

They are biomimetic properties in the sense that they mimic similar reaction-driven properties from biological functional organs. Thus, volume variations driven by ATP reactions give muscular contraction. Reactions originate electrical discharges from electric organs in fishes. Glands accumulate specific chemicals that are liberated under brain control. Synapses originate communication between neurons through ionic pulses. Ion channels in membranes originate the ionic exchanges between the intracellular matrix (ICM) and the extracellular matrix (ECM). Chemical and electrochemical potentials linked to conformational movements originate biosensors. Hydrophobic or hydrophilic skins constitute water repellent or wettable surfaces and skins.

Mono-functional and multifunctional electrochemical and biomimetic devices.

Biological organs are chemical-driven devices. Each of the composition dependent properties from conducting polymers supports the construction of a correlated biomimetic tool. Some of the reactions 8 to 11, according with the constituent polymer, will control the device actuation, like biochemical reactions control the actuation of functional organs.

Based on reaction-driven volume variations actuators, polymeric motors or artificial muscles are being developed.^{15,92,95,158–164} The final aim is the construction of zoomorphic or anthropomorphic tools and robots.

The reversible control of light absorption or light reflection (UV, vis or IR) by electrochromic films is allowing the development of smart windows, mirrors or optical filters.^{38,141,142,165}

Reactions 8 to 11, according with the constituent electrode, control the charge/discharge of all organic batteries for fast charge/discharge, and supercapacitors.^{45,145,148}

The same reactions store ions (anions or cations) in the material, which are liberated by the reverse reaction under control of the driving current. Ions having medical, neurological, fertilizer or chemical interest can be selected to be stored. The stored ions are liberated under charge control (faradaic reaction) constituting smart drug delivery, fertilizer delivery, electron-ion transducers at low potential or artificial chemical synapse devices.

Different oxidation states (different polymer/ion content) attained under control of those reactions mean different swollen states of the polymer film. When used as a membrane the transversal ionic conductivity changes under control of the oxidized state in a reversible way. The oxidized and swollen state can be tuned to allow the flow of small ions hindering that of larger ions present in the same solution, or to allow the flow of all of them with very different diffusion rates.^{152–154}

The system constitutes a smart membrane, smarter than any membrane from today's technologies and much close to biological membranes with ion channels.

The oxidation/reduction of conducting polymers include ionic diffusion processes and conformational movements of chains. Biosensors present sensitivities and selectivities several orders of magnitude higher than any chemical or physical sensor from nowadays' technologies. Present technological sensors are based on diffusion processes. Now we have the opportunity to develop chemical and physical sensors including conformational changes. New biomimetic sensors with sensitivities several orders of magnitude over nowadays sensors are expected.

By the first time we can get, in a very reproducible way, different states (different polymer-counterion contents) of conformational compacted energy. Every conformational compacted state constitutes an electro-chemo-conformational energetic memory.^{17,166} The reversible electrochemical driven conformational compaction/relaxation gives electrochemical responses including electrical information (current and charge flow), chemical information (ionic flow) and conformational

energetic information. New electro-chemo-conformational computers can be envisaged able to treat several orders of magnitude more information than nowadays computers with lower energetic consumption. Electrochemical responses from electro-chemo-conformational memories reproduce those observed from ion channels in synaptic events. A new hypothesis can be stated for one of the components of brain memory: electro-chemo-conformational memories in ion channel proteins.

Reactions 8-10 change, under control, the interaction forces (polymer-polymer, polymer-anion, polymer-cation, polymer-solvent, anion-solvent, cation-solvent and anion-cation) inside the reacting gel. Any electrochemical response from the conducting polymer, or from any electrochemical device including the polymer, must provide quantitative information related to the variation of the intermolecular forces during reactions in biomimetic dense gels. Any theoretical model developed from those experimental results could be applied to similar reactions in living cells originating health or illnesses. The reaction also changes the ionic, or the organic nature of the material composition. This fact allows changing the hydrophilic/hydrophobic nature (water-polymer interaction forces) of any surface coated with a conducting polymer or designing powder repellent surfaces.^{8,9,118-120}

Reactions 8, 9 or 10 open, in addition, an unexpected new technological world: they change, simultaneously, several composition dependent properties opening the way to develop electrochemical-driven multifunctional devices. Two or more of the above described reaction-based tools work simultaneously in a physically uniform device driven by the same imposed current, which controls the driven reaction rate.

Sensing-actuators are the first of the multiple possible two-tool devices to be developed and theoretically described: sensing artificial muscles,^{167,168} tactile artificial muscles^{92,169} and proprioceptive artificial muscles.^{93,94,170,171} Both, sensing (potential or electrical energy) and actuating (current or charge) magnitudes are present, simultaneously in the only two connecting wires. One actuator and several sensors (thermal, mechanical, chemical, electrical) work simultaneously in one physically uniform device. In nowadays technologies it does not exist any parallel multi-tool device, only biological organs (haptic muscles here) originating proprioception, awareness and consciousness can inspire such simultaneous multifunctionality.

Property's magnitude shift: faradaic model.

The actuation of any of those devices is driven by one of the electrochemical reactions 8, 9 or 10. Thus the magnitude increment of each composition dependent (through Eq. 6) polymeric property changing under reaction control must be, according with the Faraday's law, proportional to the involved charge (Q):

$$\Delta V \equiv \Delta A \equiv \Delta R \equiv \Delta q \equiv \Delta n \equiv \Delta p \equiv \Delta E \equiv \Delta U \equiv \Delta s \propto kQ \quad (11)$$

Where \equiv means as well as and \propto means proportional to, ΔV is the change of the polymer volume; ΔA , is the absorbance variation; ΔR , for the membrane reflectance variation; Δq is

the change of the stored charge; Δn , for the number of stored or liberated ions; Δp , for the film porosity (ionic diffusivity and ionic conductivity) variation; ΔE , for the membrane potential shift; ΔU , for the consumed energy and Δs , for the wettability, or other surface properties, variation; k is a specific constant for each property representing the magnitude of the property variation per unit of charge involved in the driving electrochemical reaction. So, the charge controls the magnitude of the property variation: the final position of a muscle; the new absorbance, or reflectance, of any electrochromic device; new stored charge; remaining stored moles of ions, or liberated number of moles; new average distance between chains and counterion diffusion coefficient (pore diameter); new gel potential; consumed energy during the transition; and new surface interactions with water, solvents or powders.

Electrochemical (faradaic) variation the property specific rate.

Any of the k constants becomes more general when referred to a mass unit (specific property) of the polymer (at a defined oxidized or reduced, for cation exchange or anion exchange polymers, state of reference). Moreover for a practical manipulation and control of the above electrochemical devices it results more convenient the control of the specific rate of the property variation, quantified by the applied current:

$$\begin{aligned} \frac{\Delta V}{wt} &\equiv \frac{\Delta A}{wt} \equiv \frac{\Delta R}{wt} \equiv \frac{\Delta q}{wt} \equiv \frac{\Delta n}{wt} \equiv \frac{\Delta p}{wt} \equiv \frac{\Delta E}{wt} \\ &\equiv \frac{\Delta U}{wt} \equiv \frac{\Delta s}{wt} \propto \frac{kit}{wt} = \frac{k}{w} i \end{aligned} \quad (12)$$

Indicating that the rate of change (muscle movement rate; absorbance, transmittance or reflectance variation rate; charge/discharge rate; ions liberation/storage or electron-ion transduction rate; average membrane diffusion rate; gel potential variation rate; specific consumed energy rate during the transition, or the variation rate of the surface interactions) must be under linear control of the applied current.

Reaction-driven conformational and structural movements: biomimetic materials

Reactions 7-9 induce the transformation of the molecular orbitals along the polymeric chain (Figure 4a). In the reduced state a σ bond exist between the neighbour carbon atoms of consecutive monomeric units: at ambient temperature the free rotation allows tens of different conformations for any oligomer chain. When the chain is in an electrolyte the free rotation and the strong polymer-polymer interactions originate a coil structure. After oxidation the generated radical-ions create a conjugated flat structure extended along several monomeric units. The chain extends to a stick like structure. If the chain is connected to an electrode the reversible oxidation/reduction controls the reversible movement of a molecular motor (Figure 4b).

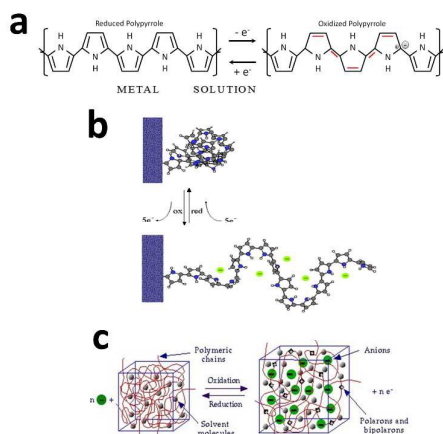


Fig. 4 (a) Electrochemical reaction 8; (b) molecular motor based on the reversible oxidation/reduction of a single polymeric chain; (c) when the chains take part of a film the reaction induced exchange of ions and solvent gives reverse three-dimensional volume variations. Reproduced from reference ¹⁶, with permission.

When the polymeric chains take part of films or powders, the reversible reaction driven conformational movements of the chains originates or destroys the free volume required to lodge/expel counterion and solvent required for charge and osmotic balance. Driven by the electrochemical reaction (7-9) and controlled by the consumed charge (Eq. 11) a reversible change of the material volume occurs (Figure 4c).

Electric pulse, chemical reaction, ionic and aqueous exchange, reaction driven conformational movements and volume changes mimic the consecutive events taking place during actuation of biological organs. Both, material content and consecutive events mimic, in its simplest expression, the intracellular matrix (ICM) content of living cells and the consecutive events originating biological functions. By the first time in Science those reactions drive reversible conformational movements and the plethora of bioelectrochemical potentialities to develop chemo-biomimetic devices. At the moment biomimetics is based on the mimesis of the extracellular matrix mechanical, physical or chemical conditions. From now on an unexplored technological world of devices driven by electrochemical and chemical reactions of the constitutive materials, as biological organs do, mimicking the ICM and its reactive biochemical functions, is emerging.⁹⁶

Electro-chemo-biomimicry.

The electrochemistry of conducting polymers, and other organic or carbonaceous materials, gives reactive gels which content and reactions mimic those taking place at the ICM of functional cells.

With the oxidation/reduction reactions the polymer/ion content of the gel changes in a reversible way under control of the consumed charge. Nowadays the only “devices” showing so large composition changes are functional cells during transition from rest state to actuation state. The value of any property of the dense gel being a function of the artificial

dense gel composition is shifted, in a reversible way, under reaction control. Any of the composition-dependent properties mimics a functional property from a biological organ: they are biomimetic properties.

Each composition-dependent property supports the development of biomimetic devices. Each device works driven by the electrochemical reactions of the constitutive material (conducting polymer), as natural organs do: they are biomimetic devices.

The ensemble reactive materials mimicking the ICM of functional cells, reactive properties mimicking biological functions and reactive devices mimicking functional organs, all of them driven by electrochemical reactions are opening a scientific and technological world: the electro-chemo-biomimicry.

Classification of electrochemical devices including conducting polymers

The electrochemical devices above indicated can be designed and constructed using one or two conducting polymer electrodes:

- Hybrid electrochemical devices: one of the actuating electrodes is a conducting polymer from any of the above families, being the second electrode an inorganic material.^{172,173}
- Symmetric electrochemical polymeric devices: the same intrinsic conducting polymer constitutes the two electrodes of the device.¹⁷⁴
- Asymmetric electrochemical polymeric devices: each of the two constitutive electrodes is a different intrinsic conducting polymer, or an intrinsic conducting polymer and a redox polymer.^{118,119}
- Full polymeric electrochemical devices. The use of a polymeric electrolyte membrane and two polymeric electrodes gives a full polymeric electrochemical device. When the two polymeric electrodes are chemically synthesised in presence of the polymeric electrolyte membrane gives interpenetrated symmetric electrochemical devices:^{175–179} the structure of the two conducting polymer electrodes interpenetrates that of the membrane electrolyte below the surface, getting a super adherent cell.

The insulator-conductor transition model for electrochemical reactions,¹⁸⁰ still very popular among electrochemists, has spread the general believe that reduced films of CPs are insulators. Most of the electrochemical devices are designed with a back metal film to support the re-oxidation of the CP films. Deep reduced thick films of conducting polymers (those required for electrochemical applications) trap up to 15% of the counterions (and polarons) involved in the film oxidation/reduction. Getting lower conductivities that 10^{-3} Scm^{-1} is a very difficult experimental task: deep reduced CP films do not need any metal support to be reoxidized.^{18,117} In addition the metal originates parallel irreversible reactions, as water electrolysis, giving lower efficiencies, contributing to the polymer degradation and decreasing the device lifetime.^{112,181}

Polymeric electrolytes and polyelectrolytes (ionic conductors and electronic insulators) are the polymeric choice for membranes in electrochemical devices and the basic material to develop full polymeric interpenetrating electrochemical devices.

Electrochemical characterization of both, materials and devices

Being the above described properties and devices based on electrochemical reactions the characterization of both, materials and devices, must start by using the three basic electrochemical methodologies: potential sweeps and their voltammetric or coulombometric responses, potential steps or square potential waves and its chronoamperometric responses and constant current or square current waves and its chronopotentiometric responses.

Electrochemical cells.

Any electrochemical device constitutes an electrochemical cell and the conducting polymer film, coating a metal or self-supported constitutes the working electrode of another electrochemical cell. Thus any material or device characterization is performed in an electrochemical cell including two (Fig. 5a-c), three (Fig. 5d) or four electrodes.

The two electrodes configuration (Fig 5a) includes a working electrode (WE), a counter electrode (CE) and the electrolyte (solvent and solvated salt, acid or base; a solid electrolyte, or an ionic liquid), which allows the current (the ions) flow between the WE and the CE. A current generator originates the flow of a constant current through the WE and the CE. A parallel voltmeter follows the evolution of the potential gradient between both electrodes. A potentiostat/galvanostat also can be used (Fig. 5b), the reference electrode (RE) output short-circuited with the CE.

When both, WE and CE are films of CPs with a thin polymeric electrolyte membrane, this is a solid electrochemical cell that reproduces any full polymeric electrochemical device (Fig. 5c). If only the WE is a CP film, being the CE a metal or semiconducting electrode, most of the cell potential gradient (and consumes most of the involved energy) is related to the electrolyte reaction at the electrolyte/CE interface. The two electrode cells does not allow the separation of the potential gradients (or the consumed energies) at the WE/electrolyte and CE/electrolyte interfaces (those producing the concomitant reactions), only allow following the evolution of the full potential gradient across the cell (WE overpotential plus CE overpotential plus potential gradient across the electrolyte) and determining the full consumed energy.

The three electrodes cell configuration (Fig 5d) moreover the WE and the CE includes a reference electrode (RE). The reference electrode is an ideally non-polarizable electrode: the electrode equilibrium reactions (forward and backward) are fast enough to support the flow of low currents without any change of the equilibrium potential. This constant reference allows determining and following the potential gradient at the WE/electrolyte interface at any time during the application of any electrochemical methodology.

The four electrodes electrochemical cell (Fig. 5e) is mainly used for the characterization of membranes of conducting polymers. A potential gradient is stated across the membrane using two RE. The auxiliary electrodes (AE) provide the required current (ionic) flow across the membrane to keep the established potential gradient. A bipotentiostat provides this current flow. Alternatively the conducting polymer membrane is used as a working electrode of a three-electrode cell to attain a new oxidation state of the membrane (a new diffusion coefficient).

Electrolyte potential window, oxidation-polymerization potential and p-doping, n-doping potential gradients.

Using a three electrodes cell configuration the potential gradient at the WE/electrolyte interface is forced to change linearly at a constant sweep rate (v , mV s^{-1}) with time from an initial potential (E_1) to a final potential (E_2) and back to the initial potential (E_1) granting the flow of the required current (between the WE and the CE) to charge the electrical double layer and to support the required reaction rates. The voltammetric (current/potential) response allows defining of the electrolyte potential window (Figure 5f), from its oxidation potential to its reduction potential. By adding the monomer the first voltammetric response gives the monomer oxidation-polymerization potential (supposed that the electrolyte oxidation potential is higher than that of the monomer oxidation). By using a self-supported CP film as WE in the clean electrolyte, the first oxidation potential, the first reduction potential, the polymer band-gap, the charge consumed for the film oxidation and film reduction during p-doping/p-de-doping or during n-doping/n-dedoping) can be obtained (Figure 5f).

Summary

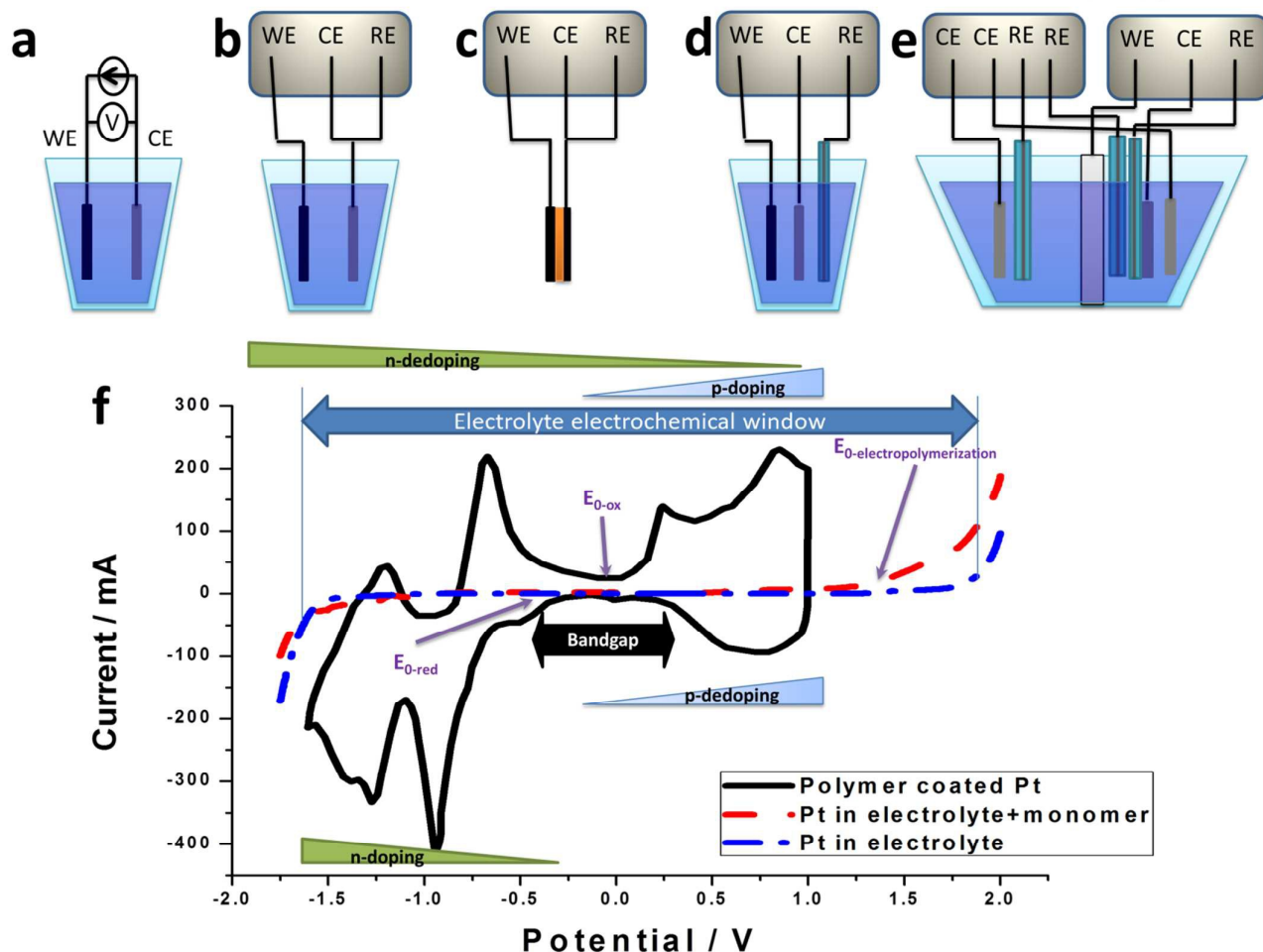


Fig. 5 (a) Two electrodes electrochemical cell, A, current generator, V voltmeter, (b) electrode's connections using a conventional potentiostat-galvanostat, (c) solid state (two electrodes configuration: CP/electrolyte/CP) electrochemical device, (d) three-electrodes electrochemical cell. (e) Four electrodes electrochemical cell used mainly for the study of CP membranes. (f) Electrolyte potential window (dot line), monomeric oxidation-polymerization (dotted line) and voltammetric response of a n-doping p-doping conducting polymer (Reproduced from reference²², with permission). Different characteristic points are indicated.

Those named conjugated conducting polymer, intrinsic conducting polymers or intrinsic electronic conducting polymers, were here distributed into nine material families (basic, substituted, self-doped, copolymers, hybrids, blends with macroanions, composites with redox carbon derivatives, other composites and salts of any of the previous families). Those materials, most of them still not synthesized, are electroactive being reversibly oxidized and reduced in presence of electrolytes. In addition redox polymers are conducting and electroactive polymers, but not bearing conjugation along the chains. The electrochemical synthesis of those materials follows a complex mechanism of parallel reactions giving a mixed material. The generally accepted polycondensation of radical cations occurs in parallel to some other reactions as: polymer oxidation, polymer degradation, chemical polymerization, branching and crosslinking. A good control of the relative kinetics allows the synthesis of tailored materials for specific applications. Once synthesized the materials follow four basic oxidation/reduction reactions in presence of electrolytes: oxidation (p-doping) with exchange of anions, oxidation (p-doping) with exchange of anions,

reduction (n-doping) with exchange of cations, and oxidation (p-doping) of the aniline family materials with exchange of protons. Charge on chains and balancing counterions force the exchange of solvent for osmotic balance. The material content (reactive chains, ions and solvent) mimics the ICM of living cells. Those reactions change, under control, the material (polymer/counterion) composition and the magnitude of the composition-dependent properties: conductivity, volume, colour, stored charge, stored ions, ionic diffusivity, intermolecular forces at the material surface, and so on. The reaction-driven properties mimic those changing in biological organs during actuation, allowing the construction of reaction-driven biomimetic devices. The fact that several composition-dependent properties of the material change simultaneously driven by the same reaction open the door for an unexplored technological word of multifunctional devices: two or more tools working simultaneously in a physically uniform device. Both, monofunctional and multifunctional devices are electrochemical cell allowing its characterization by electrochemical technologies.

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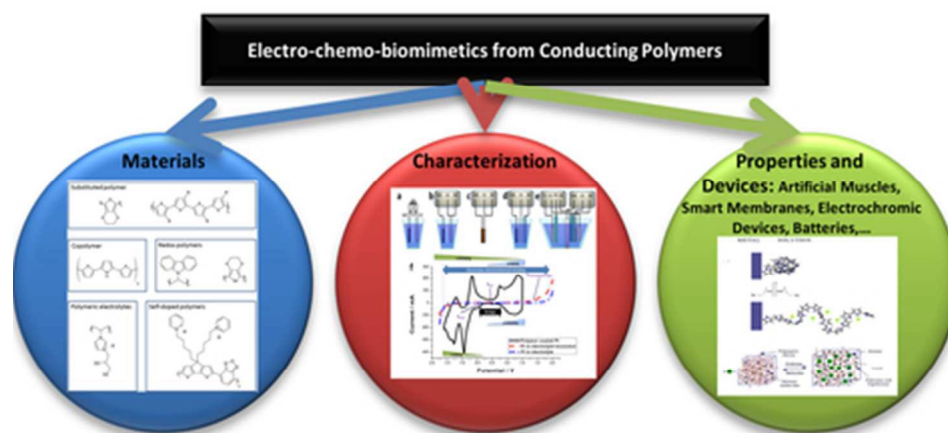
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