

Rise and rise of conducting polymers

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Abstract The discovery or, in a certain extent, rediscovery of polymers possessing high electronic conductivity launched a new field of research about 30 years ago. Electrochemistry has played a significant role in the preparation and characterization of these novel materials, which has served as a basis for many advanced applications in different areas spanning from the energy technologies to the health care. In this paper is intended to give a short summary of the history of this field, and based on the achievements until now—knowing the present limitations and opportunities—the tasks for the future are also discussed. In such a recapitulation, it is appropriate to mention the researchers who substantially contributed to the development of our present knowledge on conducting polymers during the past decades.

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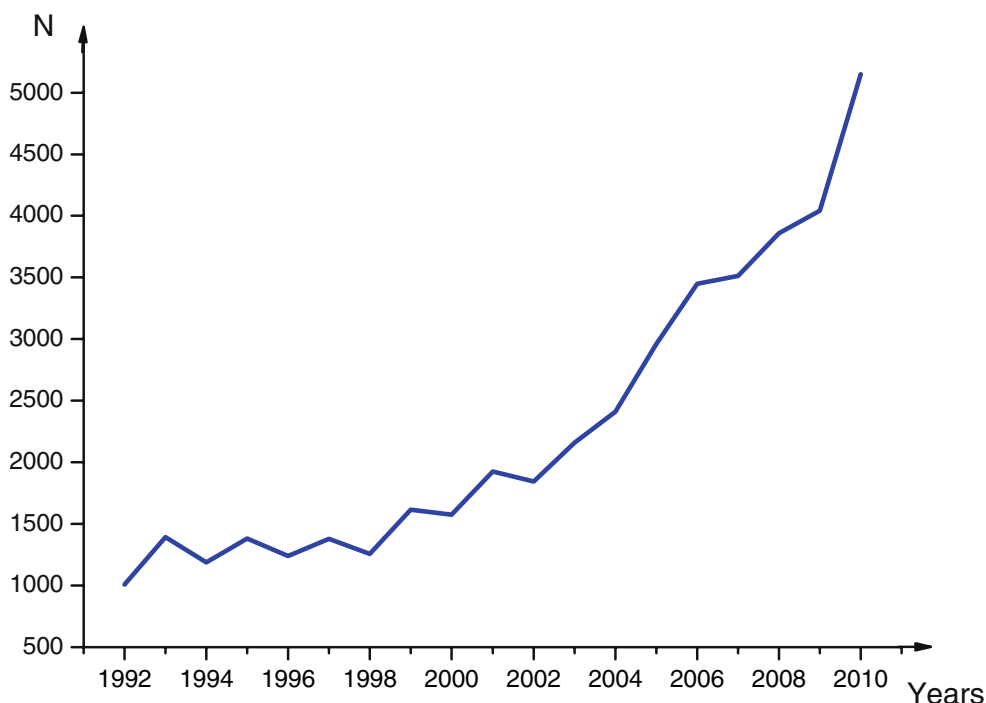
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Introduction

Conducting (conductive) polymers have encompassed a very wide field of electrochemical research, which led to numerous new applications in different areas in the last 30 years. We will focus on electronically conducting polymers (ECPs; shortly conducting polymers) and only the redox polymers will be mentioned. The number of electrochemical papers and patents on conducting polymers is very high. A search for different conducting polymers by name is instructive with respect to the importance of the polymers. The highest number can be found for polyaniline (46%), followed by polypyrrole with 34%, and polythiophene with 18%. All other polymers, e.g., polyindole, polycarbazole, polyfurane, poly(*o*-phenylene diamine), play a minor role in comparison with the polymers mentioned above. A narrow search at ScienceDirect for related papers in scientific journals produced a total of 49,615 hits. The number of papers shows an increasing trend as presented in Fig. 1.

Because many recent and old books, monographs [1–23] and reviews [24–45] on this topic are available, it is not the author's intent to go into details. However, it is essential to deal with conducting polymers, when the past, present and future of electrochemistry are surveyed in 2011. Electrochemistry has played a fundamental role in the preparation and characterization of these materials. Naturally, we will also deal with the most important applications since it is the ultimate goal of the efforts of thousands researchers who have been working in this fascinating field. There are still several limitations in the

Fig. 1 Number of papers published (N) during the last 18 years. (Before 1991, the total number was 8174.) Data taken from ScienceDirect. Because in this search mostly Elsevier publications are considered, the real number is much higher



use of conducting polymers, which have to be overcome. It is the task for the future.

Very deep is the well of the past

The story started in the 1970s when somewhat surprisingly a new class of polymers possessing high electronic conductivity (ECPs) in partially oxidized state was discovered. The three collaborating scientists, Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa, played a major role in this breakthrough, and they received the Nobel Prize in Chemistry 2000 “for the discovery and development of electronically conductive polymers”.

However, different conducting polymers had already been prepared. Henry Letheby—as early as 1862—prepared polyaniline by anodic oxidation of aniline, which was conductive and showed electrochromic behavior [46]. F.F. Runge (1834) and C.J. Fritzsche (1840), who isolated aniline, also observed the appearance of blue color during oxidation of aniline in acid media. Fritzsche analyzed the material which was called “aniline black” [47]. In 1935, Yasui [48] suggested a reaction scheme for the electrooxidation of aniline at a carbon electrode. Khomutov and Gorbachev [49] took the next step in 1950 by discovering autocatalysis during the electrooxidation of aniline. In 1962, Mohilner et al. [50] reinvestigated the mechanism of electrooxidation of aniline in aqueous sulfuric acid solution at a platinum electrode. They proposed a free radical mechanism, and they wrote that “the final product of

this electrode reaction is primarily the octamer emeraldine, or a very similar compound”.

In 1967, Buvet delivered a lecture at the 18th meeting of CITCE (later ISE), the presentation of which appeared a year later in *Electrochimica Acta* [51]. We cite the first sentence of this paper, which speaks for itself: “Polyanilines are particularly representative materials in the field of organic protolytic polyconjugated macromolecular semiconductors, because of their constitution and chemical properties”. de Surville et al. also established that “polyanilines are also have redox properties” and “the conductivity appears to be electronic”. It was also shown that “polyanilines are also ion-exchangers”. Finally, they proposed that “polyanilines ... can be utilized for making accumulators with organic compounds”. While de Surville et al. [51] used chemically prepared PANI pellets as an electrode and for the conductivity measurements, the study of the mechanism of the electrochemical oxidation also continued [52], and the name polyaniline has been generally accepted [53]. The study of Diaz and Logan [54], which was reported in 1980, has initiated the research of polymer film electrodes based on polyaniline. We also cite the stories of polypyrrole and other conducting polymers similarly, e.g., Bolto et al. [55, 56] reported conductivity in iodine-doped polypyrroles. This group reported resistivities as low as $0.03 \Omega \text{ cm}$. In fact, the career of polypyrrole started in 1979 through the work of Diaz et al. [57–59]. Nevertheless, the polyacetylene prepared by Shirakawa and co-workers, and whose high increase of conductivity after “doping” was discovered by the group led by MacDiarmid and Heeger, actually launched this new field of research [60–65].

Major efforts in the 1980s and 1990s

Electrochemistry has played a significant role in the preparation and/or characterization of these novel materials from the very beginning. Electrochemical techniques are especially suitable for controlled synthesis of ECPs by electropolymerization and for tuning of a well-defined oxidation state of both the ECPs and redox polymers. There were at least two major reasons for the intense interest of electrochemically active polymers in the early years. The first is the intellectual curiosity of scientists that focuses on understanding the behavior of these systems, in particular on the mechanism of charge transfer and charge transport processes occurring in the course of redox reactions of conducting polymeric materials. Second is the wide range of promising applications in the field of energy storage, electrocatalysis, organic electrochemistry, bioelectrochemistry, photoelectrochemistry, electroanalysis, sensors, electrochromic displays, microsystem technologies, electronic devices, microwave screening, corrosion protection, etc. The first steps have been directed towards the clarification of the nature of charge propagation, i.e., the transport of electrons to a relatively large distance. At the end of 1980s, the basic mechanisms have been established, i.e., the electron transport occurs via an electron exchange reaction (electron hopping) between neighboring redox sites in redox polymers and by the movement of delocalized electrons through conjugated systems in the case of electronically conducting polymers (also called intrinsically conducting polymers [ICPs], synthetic metals) such as polyaniline or polypyrrole. In fact, several conduction mechanisms, such as variable range electron hopping and fluctuation-induced tunneling, have been introduced, and besides the intrachain conduction these processes are considered for nonintrinsic (interstrand and interfiber) conduction processes in ICPs. Electrochemists have started to use the band models elaborated by the theoretical physicists and to speak of polarons and bipolarons as charge carriers. According to this perception after oxidation, conducting polymers exhibit localized states in the bandgap. These states are positively charged (i.e., they are “holes”) because an electron has been removed. We say that the states are “localized” because they span only a few monomer units. Interestingly, the electrical species (the positive hole) causes a structural disturbance to occur around itself, which then hinders the motion of the hole. This combination of hole and structural disturbance is jointly called a “polaron”, because the hole has polarized its environment. Polarons are very important because, at room temperature, they can conduct electrical current along the polymer backbone. Besides causing conductivity to ensue, localized states in conducting polymers also cause visible light to be absorbed (electrochromism). In almost every case, the charge is also carried by the movement of electroinactive

ions during electrolysis, i.e., these materials constitute mixed conductors. It has also been realized that other processes strongly influenced the performance of these systems: among others, chemical changes (dimerization, cross-linking, ion-pair formation, etc.) also occur and polymeric properties (chain and segmental motions, changes in the morphology, slow relaxation) play an important role. During this period, many polymers have been prepared, and it became clear that at each system new problems arise. Although the conductivity of polymers is interesting and a utilizable property in itself, the essential point is the variability of this conductivity, i.e., the easiness of reversible switching of these materials between their insulating and conducting forms.

Polyacetylene has major drawbacks, most notably it is unstable in air; consequently, even the discoverers of this material started to deal with other polymers. MacDiarmid’s attention has turned to polyaniline in 1985 [66], which showed interesting properties (proton doping, nice and fast color change, high stability even in concentrated acid solutions, etc.); it was also easy to prepare from cheap aniline both via electropolymerization or chemical polymerization by using suitable oxidizing agents. Aside from investigation of basic properties such as protonation later, his group fabricated electrically conducting nanofibres of a polyaniline blend for the applications in nano electronic devices.

Heeger, collaborating with Wudl, started to work with polythiophene and derivatives such as poly(*iso-p*-thionaphthene), with the objective of probing how to tune electronic properties via the molecular structure. By 1987, Heeger’s team had made the first inroads into device applications—making a diode by casting a polythiophene from solution onto electrodes. Heeger remained a major player in the field of light emitting polymer diodes; he is among the most cited authors in the area of conducting polymers [67]. In 1990, Heeger and colleagues started a company, UNIAX, to steer conducting polymer technology towards commercialization. Nevertheless, other scientists have played more important roles in this area during the 1980s and 1990s than the future Nobel Prize winners especially in the electrochemical preparation and investigation of conducting polymers. Polythiophene was prepared first in 1982 [68] within a year after the two other, still most popular, polymers, the polypyrrole (1979) and polyaniline (1980). It should be emphasized that when we speak about a polymer we think of all its derivatives. Another noteworthy point is that the monomer used in the course of polymerization is not necessarily the name-giving compound; it can also be the respective oligomer. It was the period when the researchers took all the possible aromatic compounds from the shelves, and tried to polymerize them. In particular, in the cases of aromatic amines and heterocyclic compounds, these efforts

were crowned with success. Neither of those showed as good behavior as the three polymers described above, but polycarbazole, poly(*p*-phenylene), poly(*p*-phenylenevinylene) and polyfluorene became useful in organic electroluminescent devices (OLEDs).

The simple cyclic voltammetric and potential step experiments have gradually been replaced by electrochemical impedance spectroscopy (EIS) and combined techniques such as electrochemical quartz crystal nanobalance (EQCN), radiotracer, probe beam deflection (PBD), spectroscopies, ellipsometry, conductometry, scanning probe microscopies. In some cases, especially in the second half of the 1990s, even further combinations (EQCN-PBD, EQCN-radiotracer) or new, more effective versions, e.g., ac EQCN, were introduced. Besides in situ methods scanning electron microscopy, X-ray diffraction and other techniques were also applied. By the help of the EQCN and radiotracer techniques the ion exchange and solvent sorption processes have been monitored successfully. EQCN provided also information about the viscoelastic properties of surface films. The continuous development of the theory of EIS led to the more accurate determination of the rate of charge transport and charge transfer processes, redox and double layer capacitances, etc., and substantially contributed to our knowledge concerning the nature of the rate-determining charge transfer step and the effect of morphology of the kinetics of the electrode reactions.

It is a very difficult to name the researchers who substantially contributed to the development of this field since it is a rather large community. Nevertheless, I think that it is appropriate to mention colleagues and their selected contributions (to save space only one to three characteristic papers). From different options, I chose an enumeration by techniques applied (introduced or developed by them) because it has been more characteristic for different research groups than the polymers investigated. Furthermore, the permanent development of theory and practice of different techniques substantially contributed to the better understanding the complex nature of the systems in question. Regarding the theory of EIS technique and the characterization of different polymeric systems, I have to mention the early works of Bard's group [69] as well as Rubinstein et al. [70] (these papers are among the most cited papers that appeared in the *Journal of the Electrochemical Society*), Deslouis et al. [71], Alberly et al. [72], Buck et al. [73], Mathias and Haas [74], Vorotyntsev et al. [75–77], Armstrong et al. [78], Láng and Inzelt [79, 80], Gabrielli et al. [81], Dunsch, Paasch et al. [82], Florit, Posadas et al. [83], Bisquert et al. [84], Fletcher [85], Pickup et al. [86] and Horvat-Radosevic et al. [87]. The most important EQCN measurements have been carried out by Buttry et al. [88], Bruckenstein, Hillman et al. [89–92], Inzelt et al. [93–95], Haas, Kötz et al. [96], Calvo et al. [97] and Gabrielli,

Cordoba-Torresi et al. [98, 99]. Radiotracer technique has been introduced by Inzelt and Horányi [100, 101], while PBD technique has been used successfully by Kötz, Haas, Barbero et al. [102] as well as by Vieil et al. [103, 104]. The in situ conductivity measurements were elaborated and applied by Wrighton et al. [105], Kankare and Kupila [106] and Vieil et al. [107]. Spectroelectrochemistry (UV–VIS–NIR, ESR, FTIR, Raman) has been extensively applied, and among the papers published in this field we mention Inzelt, Chambers et al. [108, 109], Cushman et al. [110], Glarum and Marshall [111], Lapkowski and Genies [112], Dunsch et al. [113, 114], Dubois, Lacaze et al. [115], Holze [116], Nekrasov et al. [117], Kankare, Visy et al. [118], Kinoshita, Kaneko et al. [119] and Sundholm, Lankinen et al. [120]; however, there are many other papers from different groups. Scanning microscopies (STM, AFM and SEM) have been used also for the study of the conducting polymer films, and reports in this field include, among others, Siegenthaler et al. [121], Compton et al. [122], Seeber et al. [123], Abrantes et al. [124], Mirkin, Bard et al. [125], Zoski et al. [126] and Mandler et al. [127]. Of course, this list is rather incomplete. Since it is focused on the techniques applied, and the scientists were grouped accordingly, I feel that I have to name several other researchers who were missing: Schultze, Tsakova et al. [128, 129], Peter, Kalaji et al. [130], Stilwell and Park [131] and Zotti et al. [132] for their work on the deposition of polymer. I should also mention Heinze et al.'s systematic studies on the electropolymerization (oligomeric approach and σ -dimers) [133, 134]; Ivaska, Bobacka, Lewenstam et al. [135], who have been working on the electroanalytical applications; Aoki et al. [136] and Otero et al. [137], in relation to the relaxation of polymer networks; Oyama, Kunitamura et al. [138], Skompska, Aurbach, Levi et al. [139] as well as Kulesza et al. [140] for investigations on composite materials; Mandic and Duic [141] for their electrocatalysis works, Karyakin et al.'s [142] pioneering work on polyazines and Pron et al. [143] for the preparation of molecular composites of functionalized polymers.

From the very beginning, substantial efforts have been spent on applications of conducting polymers in the areas mentioned above, and the pace certainly accelerated at the second half of 1990s, when enough knowledge has been accumulated regarding the general behavior of conducting polymers as well as the detailed characterization of each system.

Further developments in the 21th century and future prospects

Until ca. 2000, the preparation and characterization of new polymers as well as the understanding of the mechanism of

the charge transport and charge transfer processes were in the foreground of research; however, simultaneously the utilization of their useful properties has also been started. In the new century, the quest of technological application came into the limelight. It is evident that for any practical use, long-term stability and processability are indispensable. The knowledge accumulated during the last two decades is a good guide concerning the opportunities and the limitations in this field. It is usually no problem to control the charging state of the polymers either by electrochemical methods or chemically. We can utilize the variation of the conductivity in electronic devices including thin film transistors and insulated gate field effect transistors or in gas sensors; the color change in electrochromic display devices or in smart windows, the electroluminescence in light emitting devices, the swelling–deswelling accompanying the charging–discharging processes in artificial muscles, the charge storage capacity in energy technologies (batteries, supercapacitors). There are properties which are useful in a certain application, e.g., volume change; however, those may cause problems in other utilizations. In fact, during the redox transformations, we generally create a polyelectrolyte from an uncharged polymer, which alter many physical and chemical properties. For instance, the charged salt form is insoluble, while the neutral form is soluble in certain organic solvents. The overcharging (overoxidation) may lead to the hydrolytic degradation of the polymer. In some cases, the mechanical properties including adhesion is of importance, e.g., in corrosion protection or in membranes where gas evolution occurs, which are less crucial in batteries. In the early period, such effects were utilized than the change of morphology, swelling by using different counterions or derivatization of the monomer which results in a more flexible polymer. In the last decade researchers have started to apply novel approaches.

The new trend is the fabrication of composites including nanocomposites of polymers and other materials such as carbon nanotubes, graphene or inorganic compounds having special structure and properties. In sensors and biosensors of different kinds (conductometric, impedimetric, potentiometric, amperometric and voltammetric), conducting polymers are used as active, sensing or catalytic layers; however, in the majority of applications those serve as matrices entrapping enzymes or other biologically active compounds. The biocompatibility of most conducting polymers provides an opportunity for their application in medicine as artificial muscles and limbs as well as artificial nerves. The biomimetic (bionic) applications certainly will continue in the future.

The keyword of the future is improvement. The use of the derivatives of monomers or copolymerization of different monomers may be an option to obtain conducting polymers, which are more flexible or rigid or even crystalline for, e.g., heterojunction solar cells, and are also mechanically and chemically more stable and have a more

advantageous processability, etc. We may think of the career of poly(3,4-ethylenedioxythiophene, PEDOT), which is still one of the most electrochemically and thermally stable conducting polymers with a low band gap energy and high electronic conductivity; it is used in many applications especially in LEDs, photodiodes and electrochromic devices [126, 144, 145], but also as a suitable biocompatible material [146]. Even a small modification can result in favorable properties, e.g., fluorinated polyanilines were found more effective in bacterial fuel cells than unmodified polyaniline because of their higher stability towards microbial and chemical degradation and increased protection of platinum catalyst from becoming poisoned by metabolic by-products [147]. The functionalization of conducting polymers which lead to smart materials interacting and responding to their environment also offers great potential. The preparation of self-doped polymers is also a good way to overcome the problems of ionic charge transport during redox switching and other limitations of the use of polymers. For instance, sulfonated polyaniline can be used also at higher pH values [148]. The other possibility is a combination of the arsenal of materials science with chemistry (electrochemistry) to improve properties for special purposes. Nanocomposites, hybrid materials based on conducting polymers, certainly will be important materials in the future. There is a high expectation concerning electroconducting nanomaterials such as nanofibers, nanorods and other nanostructures based on the supramolecular self-assembly of conducting polymers, e.g., in the enhancement of the photoluminescence efficiency by utilization of the energy and charge transfer effect in surface resonance coupling. Manipulation of the microstructures of polymers may improve the performances of both polymer-based transistors and electrochemical cells. There will be tasks for chemists and electrochemists in the production and characterization of new materials, for the theoreticians to explain the phenomena observed or will be observed and to predict new opportunities, and engineers to give a final form of the devices. Conducting polymers are relatively cheap materials; however, the specially improved properties can give a further boost concerning mass production, which makes products considerably less expensive. For instance, making ink from conducting polymers opens up new horizons for printing sensors, electronic circuits, solar cells, light emitting displays, etc. It should also be emphasized that the theories need further development since the charge transfer and charge transport processes within a polymer chain or in a polymer layer are not perfectly elucidated yet, due to the complexity of these systems.

The new trends can be nicely followed by studying the literature, including papers and topics of conferences. There have been many specialized meetings in the last three decades, and special issues of journals devoted to conducting

polymers. The International Society of Electrochemistry established a separate division of conducting polymers, which existed for ca. 10 years. A series of workshops entitled “International Workshop on Electrochemistry of Electroactive Polymer Films” has started in 1995, which was held in different countries in every 3 years. In the last decade, however, “polymer films” were replaced by “materials” in the title—indicating that materials science, composites, hybrid materials have gained importance in this field, and the electrochemical behavior of these electrochemically active materials can be explained by the theories derived for surface polymer films.

It is certainly a joint effort of theoretical and experimental chemists (electrochemists!) and physicists as well as engineers to develop further the fundamentals and the applications of conducting polymers to gain a deeper scientific understanding and to develop usable, economically competitive products that will meet societal needs in energy storage and conversion (solar cells, fuel cells, batteries), health care (sensors, controlled drug delivery), and many other areas which have been already mentioned. We may expect a continuously improving performance of the new devices due to new scientific and technological advances, among others the introduction of new materials, improved materials engineering, and more sophisticated device structures.

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