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Review

Electrochemically synthesised conducting polymeric materials for applications towards technology in electronics, optoelectronics and energy storage devices

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Abstract

The state of the art of novel electronically conducting polymeric materials is presented in this review. The special emphasis is laid on the electrochemical synthesis of conducting polymers (CPs) including the choice of the monomers and solvents, supporting electrolytes and electrodes and structural aspects of these novel materials and the nature of the dopants which induce electrical conductivity in conjugated organic polymers. Finally, an overview of various technological applications of these novel polymeric materials to electronics, optoelectronics devices like electrochromic cells, light emitting electrochemical cells and photoconducting devices, solar cells such as photovoltaic and photoelectrochemical (PEC) cells, p-n-semiconductors, metal-insulator-semiconductors (MIS), laser materials and energy storage applications like solid-state rechargeable batteries and supercapacitors has been presented. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Since the discovery of much of the new exciting chemistry and physics in the field of conducting polymers [1-3], it is possible to control the electrical conductivity of polymer over the range from insulating to highly conducting (metallic) state. This process is often referred to as 'doping'. The insulating neutral polymer is converted into an ionic complex consisting of a polymeric cation (or anion) and a counterion which is the reduced form of the oxidising agent (or the oxidised form of the reducing agent). In the solidstate physics terminology, the use of an oxidising agent corresponds to p-type doping and that of a reducing agent to n-type doping. The oxidation or reduction of the polymer can be achieved electrochemically by subjecting the neutral polymer to the appropriate oxidising or reducing voltage in an electrochemical cell. The charge appearing on the polymer chain is then neutralised by a counterion from the electrolyte solution. An interesting group of conducting polymers consists of those prepared by the electrochemical oxidation and simultaneous polymerisation of some monomers which react at the anode of an electrochemical cell. This group includes polyaniline, polypyrrole, polythiophene, poly p-(phenylene vinylene), poly p-phenylene and their derivatives. A variety of applications towards technology of these materials has been proposed and demonstrated, viz. rechargeable batteries, electrochromic displays and smart windows, light emitting diodes (LEDs), toxic waste cleanup, sensors, corrosion inhibitors, field effect transistors (FETs), electromagnetic interference (EMI) shielding etc.

2. Importance of molecular electronics and molecular engineering

The latest trends in increasing the density and complexity of semiconductor chip circuitry have stressed the need of developing new revolutionary semiconductor technologies which might be based on totally different class of materials. One possible class of materials which may meet the above trends and may find applications in electronic industry is organic conductors and semiconductors. In fact, the replacement of traditional inorganic semiconductors by organic

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molecules, polymeric or even biological materials has recently been termed as 'molecular electronics'. Molecular electronic materials can offer viable alternatives to the traditional inorganic materials in many applications because of their extremely small size, abundance, diversity, ease of production, fabrication and potential high performance/lowcost.

Additionally, in molecular electronics, the electronic and/ or optical properties are locked into the molecular structure instead of being produced by the fabrication or processing technique. This unique feature called molecular architecture or molecular engineering ensures a suitable control on the electronic/optical properties of a resulting device by altering/modifying the organic molecular structure before fabricating the actual device.

The electrochemical synthesis of conducting polymers, first unraveled with polypyrrole, has proven important in allowing development of new polymeric materials with similar electrochemical and/or electrical properties. According to this approach, semiconducting polymers have been obtained from a wide variety of monomers which include thiophene, furan, carbozole, aniline, indole, azulene and polyaromatic monomers such as pyrene and fluoranthene.

In this 'polymer age' of today, tremendous advancement has been made in developing various polymeric materials which are fast replacing the conventional materials such as metals and alloys in number of applications, thus bringing about cost-effectiveness, reduction in size and weight, new designs and in fact entirely new concepts in materials science. In particular, metals have been replaced by plastics in many fields such as automobiles, aerospace, light engineering machinery, household goods, electronics etc. This has been possible because of the various mechanical properties which can be tailored into the polymers by a number of processing techniques. However, there still remains a field where polymers have to enter and that is in electrical conductivity in which metals still have an upper hand. Nevertheless, this situation may not last long since rapid advances are taking place in the past couple of years in the synthesis of conducting polymers. Amongst the different techniques of making polymers conductive, that of composite formation (i.e. mixing the polymeric materials with fillers that are conductive such as carbon black, acetylene black, carbon film, metal powders, flakes etc.) has already been commercially exploited.

There are number of drawbacks in such filled materials (fillers), namely (a) their conductivity is highly dependent on processing conditions (b) often an insulating surface layer gets formed (c) and the articles may become brittle because of heavy loading of filler.

In order to overcome these together with the need to extend the application areas to microelectronics, the polymers have to be made inherently conductive. This can be achieved by modifying the basic chemical structure or by doping at the molecular level. The field of molecular electronics thus has emerged. Table 1 shows the potential applications of conducting/semiconducting polymers in a variety of devices.

3. Conducting and semiconducting polymers – the latest development

Conducting and semiconducting polymers have received immense attention since the discovery of high conductivity

Ta	bl	le	1

Applications of conducting polymers in device

Conducting polymers	Device application
(A) Polyaniline and substituted polyaniline	 (1) Electrochromic display (2) Photolithography (3) Rechargeable battery (4) Electrochemical capacitors (5) Corrosion inhibitors (6) Sensors
(B) Polypyrrole and substituted polypyrrole	 (1) Electrochromic display (2) Light weight battery (3) Sensors (4) Solar energy cells
(C) Polythiophene and substituted Polythiophene	 (1) Electroluminescence (2) Electrochemical capacitors (3) Cathode materials for battery (4) Microlithography (5) Corrosion inhibitors
(D) Poly-p-phenylene (PPP) p-phenylene vinylene (PPV)	 (1) Electroluminescence (2) Photoconductors (3) Solar energy cells (4) Laser materials

Table 2 Maximum conductivity and type of doping of some important conducting polymers

Conducting polymer	Maximum conductivity (S/cm ²)	Type of doping
Polyacetylene (PA)	200-1000	n, p
Polyparaphenylene (PPP)	500	n, p
Polyparaphenylene sulphide (PPS)	3–300	р
Polyparavinylene (PPV)	1-1000	p
Polypyrrole (PPY)	40–200	p
Polythiophene (PT)	10–100	p
Polyisothionaphthene (PITN)	1–50	p
Polyaniline (PANI)	5	n, p

in doped polyacetylene [4]. It should be noted that polyacetylene was first synthesized sometime ago [5]. However, metallic conductivity in this polymer has been reported only in 1977 when it was doped with iodine and other molecular acceptors. Although polyacetylene remains one of the most studied conducting polymers of today, its inherent instability in air and the tedious processability have motivated the research on other stable and easily processible polymeric materials based on polyheterocycles having five membered ring structure in the main chain. These polymers (viz. polypyrrole, polythiophene, polyfuran etc.) have greatly dominated the field of conducting and semiconducting polymers. This can be specifically associated with the emergence of advancements made in electrochemical polymerisation (ECP) technique which is a fast developing field interfacing polymer science and electrochemistry. It provides a novel approach to the synthesis of conducting polymers.

In this over-view,

- we wish to describe the ECP process, its uniqueness and attractive features.
- Provide some aspects of R&D activities with particular emphasis on applications towards technology in devices electronic/optoelectronic and energy storage.

Table 2 gives maximum conductivity and type of doping (n or p) for some of the more important conducting polymers.

4. Electrochemical polymerisation process (ECP)

4.1. Set-up

ECP is normally carried out in a single compartment electrochemical cell by adopting a standard three electrodes configuration (discussed in Section 4.4) typical electrochemical bath consists of a monomer and a supporting electrolyte dissolved in appropriate solvent. ECP can be carried out either potentiostatically (i.e. constant voltage condition) or galvanostatically (i.e. constant current condition) by using a suitable power supply. Potentiostatic conditions are recommended to obtain thin films while galvanostatic conditions are recommended to obtain thick films [6]. A general set-up for ECP process is given in Fig. 1.

4.2. Choice of monomers

The compounds which possess relatively lower anodic oxidation potential and are susceptible to electrophilic substitution reaction can produce conducting polymers by electrochemical technique [7]. Table 3 gives peak oxidation potentials of some of the aromatic compounds.

The Table 3 shows that the electrochemically polymerisable monomers reported so far have peak potentials below 2.1 V. Low peak potential avoid complications in the polymerisation arising from the oxidative decomposition of the solvent and the electrolyte. Also, all the monomers



Fig. 1. General set-up for electrochemical polymerisation.

 Table 3

 Electrochemical data for some heterocyclic and aromatic monomers

Monomer	Oxidation potential (V) Vs. SCE
Pyrrole	1.20
Bipyrrole	0.55
Terpyrrole	0.26
Thiophene	2.07
Biothiophene	1.31
Terthiophene	1.05
Azulene	0.91
Pyrene	1.30
Carbazole	1.82
Fluorene	1.62
Fluoranthene	1.83
Aniline	0.71

(mentioned in Table 3) being aromatic in nature undergo electrophilic substitution reaction by maintaining the aromatic structure. Monomer such as phenol, which are otherwise difficult to polymerise get converted into polyphenylene oxide (PPO) by ECP process [8,9].

4.3. Choice of the solvent and supporting electrolyte

Since the electrochemical polymerisation reaction proceeds via radical cation intermediates, nucleophilic character of the solvent and electrolyte imposes certain restrictions on their choice [7]. Aprotic solvents (viz. acetonitrile, benzonitrile, etc.) with poor nucleophilic character are preferably used for this reason. However, certain nucleophilic aprotic solvents such as DMF, DMSO and hexamethyl phosphoramide and hydroxylic solvents can also be used if the nucleophilicity of the solution is reduced by the addition of suitable protic acid.

The choice of supporting electrolyte depends upon the solubility, degree of dissociation and nucleophilicity criteria. Quarternary ammonium salts of the type R₄NX (where R = Alkyl, Aryl radical and X = Cl^- , Br^- , I^- , ClO_4^- , BF_4^- , PF₆⁻, CF₃SO₃⁻, CH₃C₆H₄SO₃⁻) are soluble in aprotic solvent and are highly dissociated in them. Such salts are, therefore, commonly used as supporting electrolytes in electrochemical polymerisation of conducting polymers. Some lithium salts are also soluble in aprotic solvents but they remain highly aggregated. Most of the sodium and potassium salts are poorly soluble in aprotic solvents. When halides are used as supporting electrolyte, good films cannot be obtained because halides are fairly nucleophilic and get oxidised easily. Highly nucleophilic anions such as hydroxide, alkoxide, cyanide, acetate and benzoate do not produce good quality films, but, instead, produce soluble products which colour the reaction bath.

4.4. Electrodes

A standard three electrode system comprises of a working electrode, counter electrode and reference electrode dipped

in a single dual compartment cell. The working electrode acts as a substrate for electro-deposition of polymers. Since the polymeric films are deposited by an oxidative process, it is necessary that the electrode should not oxidise concurrently with the aromatic monomer [7]. For this reason only, inert electrodes like Pt, Au, SnO₂ substrates, ITO and stainless substrates are used. A counter electrode which is a metallic foil of Pt, Au and Ni, is used sometimes. A reference electrode like saturated calomel electrode (SCE), Ag/AgCl electrode etc., can be used.

4.5. Attractive features

The ECP technique has several attractive features mentioned as follows;

1. Supporting electrolyte used in electrochemical polymerisation serves two purposes.

(a) It makes electrolytic bath solution conducting and(b) It dopes the polymer by allowing one of its ions to couple with monomer unit.

Much wider choice of cations and anions for use as 'dopant ions' becomes available in electrochemical polymerisation if we select the appropriate electrolyte. This is the most important feature of this technique.

2. The most salient feature of electrochemical polymerisation, is that polymerisation, doping and processing take place simultaneously while in conventional method, first polymer synthesis is carried out which is subsequently followed by doping and processing.

5. Research and development - some aspects

5.1. Historical background

The pioneering work of Diaz et al. [10] on electrochemically prepared conducting polypyrrole has triggered a new era of research for both polymer chemists and material scientists. As a consequence, many reports dealing with electrochemical preparation and characterisation of conducting polyheterocycles (particularly polypyrrole and polythiophene) have been appearing in the literature. In order to get a fairly detailed account of R&D activities in this field, one can always refer to some of the available reviews. For example, the work on electrochemically prepared polypyrrole upto 1983 has been reviewed by Diaz and Kanazawa [7]. The results on electrochemically prepared polythiophene and polyisothionapthalene have been reported by Wudl and his coworkers [11]. Malhotra et al. [12] have published a comprehensive review on the studies of electrochemically synthesized polyheterocycles.

Most of the researchers in this field have emphasized on the immediate applications of electrochemically synthesized conducting polymers particularly polypyrrole, polythiophene in battery technology and possible applications in electronic/optoelectronic devices like solar cells [13], photoconductors [14,15], electrochromic displays [16], FETs [17,18] etc. The increasing number of papers on electrochemically produced conducting/semiconducting polymers devoted to all the facets of this subject convincibly indicates that the possibility of obtaining a feasible and an 'all-polymer' based electronic device comparably efficient to conventional ones is not too remote.

5.2. Current state of art and future scope

5.2.1. General remark

In order to utilise the conducting polymers for electrical/ electronic devices, one has to look into various characteristics like current–voltage change, storage and degradation for these materials.

5.3. Advanced polymeric materials

5.3.1. Novel materials and structural aspects (polymer, polymer derivatives, co-polymers, graft co-polymers, polymer composites, etc.)

At present, all the R&D efforts in this field have been mainly concentrated upon polyheterocycles like polypyrrole, polythiophene, polyfuran, polyisothionapthalene, polyindole, polyaniline, polycarbozole etc., and polyaromatics like polyazulene, poly-p-phenylene (PPP), poly p-phenylene vinylene (PPV) and polypyrene etc. It is now established that the π -electron conjugation along the backbone of polymer chain is one of the criteria for a polymer to exhibit good electrical (conducting and semiconducting) behaviour and all of the above mentioned materials fulfill this criterion. Additionally, it is also known that the presence of heteroatom in polymers can lead to improved electrical (conducting/semi-conducting) performance. In principle, a variety of new functional polymers can be synthesized electrochemically by starting with appropriate monomer units possessing π -electron conjugation and a heteroatom.

Amongst these conjugated polymers, the polythiophene (PTh) and their derivatives are well-known candidates for their 'good' electronic conductivity and stability [19–21]. In order to obtain suitable physicochemical properties of polythiophene, different chemical and electrochemical methods are employed. As the properties of polythiophenes can be influenced by their structural details, it becomes essential to understand their structural characteristics.

Electrochemical and chemical polymerisation of thiophene in a microemulsion medium using anionic surfactant was carried out by Vadivel Murugan and his coworkers [22,23]. They observed a free standing dark film of polythiophene. Eventhough chemically synthesized PTh free standing film is amorphous, the ex-situ X-ray diffraction (XRD) patterns after heat treatment (in N₂ atmosphere) upto 608° C reveal that the PTh molecules dissociated to form possibly sexithiophene (6T) and within orderly arrangement to conform to a crystalline material. The phase transformation of amorphous (PTh) \rightarrow crystalline (6T) was observed and the degree of crystallinity is calculated to be 78% [22,23] and it is air stable.

Recent studies have revealed that the appropriate substitutions in the starting monomer can improve the air stability of the electrochemically produced polymers. For example, Tourillon et al. [24,25] have reported better air stability in poly(3-methyl thiophene) than that of polythiophene both being produced under similar electrochemical conditions. The poly(3-methyl thiophene) is more conducting than the parent polythiophene [26]. This increase in electrical conductivity has not been observed in the analogous pyrrole system where the methyl substituted polypyrroles have lower conductivities than the parent polypyrrole [27]. Apparently, there is a delicate balance between electronic and steric effects, which makes substituted polymers of the five membered heterocycles either more or less conducting than their parent polymers [28,29]. Sato et al. [30,31] have shown that the electrochemical polymerisation of long-chain alkyl substituted thiophene and pyrrole yields highly conducting films, some of which are soluble in common organic solvents in their conducting state. Such discoveries may solve some of problems encountered in the characterisation (viz. molecular weight determination) of the conducting polymers.

Most of the conducting polymers produced so far by electrochemical technique exhibit poor mechanical strength which unfortunately forbids their usage in commercial products. It has been experimentally demonstrated that the co-polymerisation is one of the most effective methods to impart the mechanical strength to the known brittle polymers. In persuing this approach, it becomes imperative to take great precision in maintaining the required high conductivity/semiconductivity of the resulting co-polymers. In this regard, co-polymerisation of the above mentioned poly-heterocycles with poly(p-phenylene sulfide) would be highly desirable because

- 1. PPS can be expected to give better mechanical strength,
- 2. It has less pronounced O_2 sensitivity,
- 3. PPS can be conveniently doped to get high conductivity.

However, at present such a co-polymerisation by electrochemical technique appears to be a challenging task owing to the difference in electrochemical oxidation potential of the individual monomers. One speculative approach to overcome this problem is to use catalyst in the electrolyte bath.

The graft co-polymerisation and composite blending are another important routes to provide atmospheric stability and mechanical strength to these conducting poly-heterocycles. Although these two routes are routinely established in the conventional methods of conducting polymer synthesis, they remain relatively less explored in electrochemical approach.

Furthermore, co-polymerisation can be also as a speculative mean to adopt traditional inorganic concepts of forming solid solutions in order to 'tailor' the desired electronic and other properties.

The various aspects of incorporation of TiO₂ in polyaniline by chemical and electrochemical techniques to study the effect of photoconducting inorganic semiconductor on thermal stability and application of a new composite as revealed by XRD powder pattern, particle size analysis, electronic spectra and thermal analysis are carried out by Gurunathan and Trivedi [32,33]. They also observed that highest efficiency of polyaniline formation is obtained at a ratio of 1: 6 of TiO₂ to polyaniline. The particle size of TiO₂ has increased during incorporation in polyaniline matrix due to the formation of definite composite. It is possible to achieve 80.6% of TiO₂ in polyaniline matrix by using colloidal TiO₂. Gurunathan and Trivedi [34] have reported that the percentage of weight loss and colour of the samples of doped PAn/TiO₂ sintered at various temperatures. It is seen that 265°C is optimum temperature where composite does not loose its conductivity. At 500°C, composite gets completely destroyed and this can be explained in terms of electronic spectra, conductivity measurements and XRD patterns [34].

 $X^{-} = CIO_{4}^{-}, BF_{4}^{-}$

POLYACETYLENE (reduction or 'n - doping '):

All these facts indicate that ample scope exists for R&D activities in the field of electrochemical synthesis of novel polymers, polymer derivatives, (monomer substitution) copolymer graft co-polymer composite, blends etc.

5.3.2. Novel dopants

The properties like structure, surface morphology, electrical conductivity and air stability of the polymers depend upon the nature and extent of doping. It should be recalled that the concept of doping in polymers is rather different from that in traditional inorganics. Quite advantageously, the electrochemical polymerisation method offers a wide choice of 'dopant' ions which are taken from the supporting electrolyte added in the electrolyte bath. Schemes of electrochemical n-doping (reduction) and p-doping (oxidation) processes of selected conducting polymers is shown in Fig. 2. This is in contrast with the conventional methods of synthesising conducting polymers where the neutral polymer is first synthesised and subsequently treated with a strong oxidant/reductant in order to produce the conducting form of the polymer. With this approach, the variety of anions/cations that can be used is more limited since



Fig. 2. Schemes of electrochemical n-doping (reduction) and p-doping (oxidation) processes of selected conducting polymers.

Table 4 List of dopant ions and their source of electrolyte^a

Dopant ion	Source (i.e. supporting electrolyte)
BF ₄ ⁻	$R_4N^+BF_4^-$, MBF_4
PF_6^-	R_4NPF_6 , MPF_6
ClO_4^-	R_4NClO_4 , $MClO_4$
Cl ⁻	R ₄ NCl, HCl, MCl
Br ⁻	R ₄ NBr, MBr
I ⁻	R_4NI , MI
AsF_6^-	MAsF ₆
HSO_4^-	MHSO ₄ /R ₄ NHSO ₄
CF ₃ SO ₃ ⁻	MCF ₃ SO ₃ /R ₄ NCF ₃ SO ₃
CH ₃ C ₆ H ₄ SO ₃ ⁻	MCH ₃ C ₆ H ₄ SO ₃
SO_4^{2-}	Na_2SO_4 , H_2SO_4
$(Et_4N^+)^*$	Et_4NPF_6
$(Bu_4N^+)^*$	Bu_4NPF_6

^a R = Alkyl; Et = Ethyl; But = Butyl; $M = Metal (Li^+, Na^+, Ag^+, K^+)$. The dopant ions marked by * are not anions.

it must be generated from the chemical oxidants/reductants [35].

Table 4 presents the list of dopant ions and their source electrolytes which are currently being used in the electrochemical synthesis of conducting polymers. It should be noted that all of these dopant ions with the exception of last two (marked by *) are anions and refer to electrochemical oxidation of the polymers at the anode. Aizawa et al. [36] have reported the first example of the reductive doping of an electrochemically synthesized polythioenylene film with cations like tetraethyl ammonium (Et_4N^+) and tetrabutyl ammonium (Bu_4N^+). They have observed a red to green electrochromism as a result of cation doping.

In short, it would be of interest to study the electrical, electronic and optical properties of the polyheterocycles which are prepared by electrochemical technique after exploring the possibility of doping with (i) novel anions (other than those listed in Table 4) and (ii) novel cations (other than Et_4N^+ and Bu_4N^+). Such studies would be highly desirable from the point of view of fabricating p–n junction and electrochromic devices.

5.4. Device applications towards technology

5.4.1. Photoconductivity

Photoconductivity involves enhancement of the electrical conductivity of the material by the absorption of a suitable photon. It finds wide ranging applications in electronics products for example autobrightness control (ABC) circuits in TV sets, camera shutters, car dimmers, street light control, autogain control in transceivers electrophotography etc. ([37] and references therein).

Commercial photoconductors of today are based almost exclusively on inorganic semiconductor like Si, Ge, CdS, CdSe, CdTe, PbS, PbSe, PbTe etc. In recent years, there has been a considerable interest in the preparation and characterisation of fundamental properties of photoconducting polymers, a prime motivation being demonstrated by use of polymer based photoreceptors in the multibillion dollar electrophotography (xerox) industry.

Ideally any polymer which possesses very high resistance in the dark but can transport photoinduced charge carriers when illuminated by a suitable photon can function as a photoreceptor element. Polymers such as poly(N-vinyl carbozole) or molecularly doped polymers have demonstrated such a photoconductivity effect. Poly(N-vinyl carbozole) is a well studied photoconducting polymer. It has been actually used in the place of traditional inorganic photoconductor in xerox machines. The ability to make large area flexible polymer films at relatively low cost accounts for the application of these materials in electrophotography. Since, poly(N-vinyl carbozole) and other molecularly doped photoconducting polymers have strong intrinsic optical absorption only in the UV region, while in practical usage, visible light is normally employed. The photosensitivity of these polymers is required to be extended in the visible region. This can be done by

- 1. The formation of a charge-transfer complex with absorption in the visible range.
- 2. Dye sensitisation with an appropriately absorbing dye (or)
- 3. use of this, contiguous sensitizing layer such as amorphous selenium.

On this back-ground, polypyrrole with bandgap of approximately 2.0 eV in its neutral state appears to be better photoconducting candidate since it possesses strong intrinsic absorption in the visible range. Surprisingly, no serious effects have been made in attempting/examining photoconductivity in polythiophene eventhough it has been reported that such films are quite insensitive to air and moisture, the most detrimental factors affecting the performance of a photoconductor. Electrochemically produced polypyrrole films (band gap 3.2 eV) after sensitisation with one of the above mentioned methods can be anticipated to exhibit good photoconductivity. Park et al. [38] have studied the doping effect of viologen on photoconductive device made of poly para vinylene (PPV).

For electrophotography applications, electrochemical polymerisation technique can be considered to have an added advantage in the sense that photoconducting polymer can be processed on the metallic object of any desired shape. The combination of a photoconductor and a liquid toner containing charged particles suspended in an organic medium together with a counter electrode gives an electrophoretic image storage and display device. It may be noted that this arrangement is very similar to the electrochemical setup described earlier with the only difference being in the suspended charged species. Such an application for the electrochemically polymerized semiconducting films appears to be quite feasible especially since most of the heterocyclic polymers have an intrinsic bandgap in the visible range.

5.4.2. Solar energy conversion

On the background of present day energy crisis, solar energy has received more attention as an alternative source of energy due to its abundance and non-polluting/nondepleting nature. Amongst the various routes of solar energy conversion, photovoltaic (i.e. increase in e.m.f. with the absorption of a suitable photon) conversion has gained a worldwide popularity owing to its potential ability to provide cheap electricity in non-transporting units. So far, only the traditional inorganic semiconductors with photosensitivity in the solar spectrum region (viz. CdS, Cu₂S, Si, GaAs etc.) have been mainly used in fabricating photovoltaic solar cells. But the current emergence of electroactive polymers, as a new class of semiconducting materials, has generated a considerable interest in the fabrication of polymer based solar cells [39]. Solar cell composed of a polymer film containing sensitizer is shown in Fig. 3. Photovoltaic devices based on conjugated polymer/C₆₀ heterojunctions have been investigated using polymers such as poly 3-alkyl thiophene (P3AT), MEH-PPV [40].

In the polymeric systems, quite analogous to inorganics, photovoltaic conversion of solar energy can be accomplished by four different ways, as discussed below.

5.4.3. p-n semiconductor junction (homo/hetero)

Chiang and his coworkers [41] reported the first all polymer p-n junction device made by pressure contact of a p-type polyacetylene film (i.e. doped with Na) with n-type polyacetylene film (i.e. doped with AsF₅). Also, Ozaki et al. [42] have fabricated a p-(CH)_x : n-ZnS heterojunction solar cell with open circuit voltage of 0.8 V. Despite of its desirable direct bandgap of 1.5 eV (matching well with the solar spectrum), the main drawbacks of polyacetylene (i.e. difficult processibility and instability towards air and moisture), necessarily direct us to go for more stable semiconducting polyheterocycles, especially electrochemically synthesized polyheterocycles. The influence of structure and electronic charges induced in poly(3-methyl thiophene) (PMeT) by the monomer concentration on the characteristics of sprayed CdS(Al)-PMeT based photovoltaic junctions has been studied [43].

As mentioned earlier, Aizawa et al. [44] have demonstrated that polythiophene can be electrochemically doped with electrolyte cations. This cation doping, in turn, leads to the formation of n-polythiophene (cation doping of polypyrrole has not been observed). Thus, anion-doped polypyrrole/polythiophene can behave as n-type semiconductor. The fabrication of p–n heterojunction diode by sequential electrochemical polymerisation of pyrrole and thiophene on a platinum substrate followed by controlled potential electrochemical doping to make the polypyrrole layer aniondoped and the polythiophene layer cation-doped. However, the utility of this p–n heterodiode as a photovoltaic solar cell has not been tested.

5.4.4. Semiconductor – electrolyte (i.e. photoelectrochemical (PEC) junction)

In general, semiconductor-electrolyte junctions are relatively insensitive to the quality of the semiconductor and are favoured over conventional solid-state junctions with regard to trapping and surface recombination. However, the fact that most of the inorganic semiconducting electrodes are susceptible to undergo photodissolution process (cathodic/anodic) has partly limited the progress of research on such junctions [45,46]. In this particular context, semiconducting polymers sound to be better candidates because the pertinent photoprocesses involve only π electrons while the backbone binding σ electrons remain intact and, therefore, photodissolution may not be a serious problem in case of polymer based photoelectrochemical systems. Additionally, the porous fibrillar microstructure of semiconducting polymers should be quite advantageous in photoelectrochemical (PEC) cells, since the electrolyte can establish an effective contact with larger surface area of the electrode.

In the past, few attempts were made in producing polyacetylene based PEC cells (electrolyte-sodium polysulfide, open circuit voltage approximately 0.3 V and short circuit current approximately $40 \,\mu A/cm^2$ at AM1 illumination). It can be seen later that the semiconducting polymer based PEC cells are receiving fresh impetus through advances in electrochemical techniques of polymer



Fig. 3. Solar cell composed of a polymer film containing sensitizer.

synthesis and doping. For example, Kamat and Basheer [47] have investigated PEC effect in a system Pt(SnO₂)/ electrochemically doped poly(p-phenylene sulfide) as photoanode and Pt foil as a counter electrode in acetonitrile and water, with and without intentionally added redox couple like methyl viologen (MV⁺²). Tomkiewicz and his coworkers [48] have reported PEC properties of electrochemically prepared (as-grown and reduced form) poly(3-methyl thiophene) in various aqueous electrolytes like KI, K_3 Fe(CN)₆/K₄Fe(CN)₆, S²⁻/S/NaOH and methyl viologen (MV⁺²). They have found that the best PEC activity can be obtained with (MV⁺²). Photoelectrochromism of Poly(n-methyl pyrrole) on n-Si semiconductor substrate surface has been performed and the possibility for optical memory has been demonstrated by Inganas et al. [49]. TiO₂ semiconductor particles have incorporated as photosensitizers into methylene blue containing polyaniline matrix and photoinduced electrochromism has been achieved by illumination with the energy corresponding to the bandgap of the semiconductor [50]. Kobayashi and his coworkers [51] have reported photooxidation of PANI by photoexcited $Ru(bpy)_3^{+2}$, since this system employed photoinduced electron-transfer between $Ru(bpy)_3^{+2}$ and methyl viologen (MV⁺²).

5.4.5. Metal-semiconductor (i.e. Scottky barrier) junction

Only few attempts were made to fabricate metal-polymeric semiconductor junctions and the other tandem configurations. The photovoltaic properties of metal/polymeric semiconductors (Scottky barrier) heterojunction and photoelectrochemical cells are reviewed by Kanicki [52].

By and large, it can be seen that all polymer based solar cells have revealed poor PV performance (as judged by efficiency, stability and figure of merit criteria). To improve upon their PV performance, much concentrated efforts have to be done in the following directions:

- 1. Synthesis of new polymeric materials (includes derivatives/copolymers or polymers doped with novel dopants) which possess direct bandgap and strong optical absorption (more precisely photosensitivity) in the solar region (1.0–2.5 eV).
- 2. Electrochemical polymerisation can play an important role in this regard, particularly in getting semiconducting polymers with desired electrical conduction (n-type or p-type) by a suitable choice of dopant ions (from supporting electrolytes).
- 3. Detailed physicochemical, electrical and optical investigation (from the point of view of solar energy) of the existing electroactive polymers like polythiophene (bandgap 2.0 eV) and poly(p-phenylene sulfide) (band gap 2.5 eV) and possessing photosensitivity in the solar region.
- 4. Better understanding of the physics and chemistry of semiconducting polymer interfaces (i.e. junctions) in the existing photovoltaic configurations.

5.4.6. Metal-insulator-semiconductor (MIS)

A number of interdisciplinary studies of polymer-metal interfaces showed that, during the early stages of interface formation, deposited aluminum atoms form covalent bonds with the carbon atoms of the X linkage in polythiophene [53]. Some investigators reported that low work function metals such as Al or Ca readily react with oxygen-containing parts of the conjugated polymer or polyelectrolyte, thus forming a thin resistive layer [54]. The first polymer to be tested as a semiconductor in a diode was polyacetylene [55]. Subsequent improvements in synthesis, stability and processability have led to numerous studies on polymeric diodes such as, for example thiophene oligomers [56-58] and poly(3-alkyl thiophene) [59-63]. These Schottky diodes, however, were made from undoped or unintentionally doped conjugated polymers having low electrical conductivity, and therefore had currents at forward bias that were limited by bulk resistance.

Banktikassegn and Inganas investigated [64] a series of polymer based structures for which one of the electrodes is a vacuum evaporated Al layer. Two-terminal devices based on junctions between p-type conducting polymers doped with large polymeric anions such as polystyrenesulphonate (PSS) and low work function metals, e.g., aluminium, show symmetrical but non-ohmic I-V characteristics [54]. For example; when poly(3,4 ethylene dioxy thiophene) (PEDOT) is doped with large polymeric anions, the Al/PEDOT contact shows a metal-insulator-semiconductor or (MS'S) type of junction where S' and S are the same chemical compounds in which the S' layer has a much lower doping content than the S layer [56,57]. The same polymer doped with small ClO_4^{-} anions gives a metal-semiconductor (MS) contact. Another polymer, namely poly ((3,4, octyl-phenyl) 2,2'bithiophene) (PTOPT) which is a derivative of thiophene shows schottky type rectification when doped with small PF₆⁻ anions and the electrical features of aluminium contacts to electrochemically polymerised polypyrrole doped with poly(styrene sulphonate). The oxidised polymer is a p-type conductor and hole polarons or bipolarons are active in transport [64]. Small dopant anions such as ClO₄⁻ were also used to determine the effect of dopant size. Currentvoltage and complex impedance measurements were carried out for characterising the electronic properties of the junction between Al and doped polymer.

5.4.7. Electrochromic display and solid-state electrochromic cell

Owing to their environmental stability, low cost and easy method of preparation, conducting polymers have played the major role in electronics and optoelectronics. One of the optoelectronic application is the fabrication of large area electrochromic devices (ECD's). Schematic representation of basis and principles of electrochromic windows and an electrochromic device using a transparent solid polymer electrolyte are shown in Fig. 4 a and b, respectively. ECD's are used in commercial sign boards, arrival/departure time



Fig. 4. (a) Schematic representation of electrochromic window based on principles; (b) basic scheme involved in an electrochromic device using a transparent solid polymer electrolyte.

tables in airports and railway stations, calculators, computers, clocks, electrochromic windows to control solar energy and any other piece of equipment that utilises the liquid crystal display (LCD). The electrochromic display devices have several advantages over the LCD devices and the colour acquired remains intact even after driving voltage pulse has been removed.

The electrochromic display device materials which change colour reversibly during the electrochemical processes of charge and discharge are called electrochromic materials. Electrochromic displays are typically assembled by combining an electrode covered with a thin layer of electrochromic materials, transparent solid polymer electrolytes and a complimentary electrochromic material as a counter electrode. If the back of the counter electrode is covered with a reflective material it will act as an electrochromic mirror [65]. Polyethylene oxide containing LiClO₄ is a good solid polymer electrolyte incorporating an anionic quinone 1-amino 4-bromo anthraquinone 2-sulfonic acid in a polyaniline matrix [66]. This modified surface exhibits colourless, green, blue, purple, colour change by sweeping the potential. Otherwise, the anionic quinone shows bright red colour in an oxidised state and is colourless in a reduced state. For making an electrochromic device, the most suitable electrode is an ITO coated transparent glass and PEO-Co-epichlorohydrin containing LiClO₄ has a desirable transparency and ionic conductivity at room temperature as a solid electrolyte and polyaniline is a electrochromic material [67]. When compared to inorganic oxide materials like WO₃, MoO₃, V₂O₅ etc.; the conducting polymers and

their composites offer low cost, easy method of preparation and 'flexible' properties. The scale-up of the electrochromic device depends upon the electrochemical behaviour of the electrolyte. The lifetime of the electrochromism can be improved by making composite films of polyaniline (PAN) or poly(o-phenylene diamine) (PoPD) with poly(pphenylene terephthalamide) (PPTA) [68]. The electrochromism of the composite film by changing the anodising potential of the film exhibits a continuous variety of colours: orange (-0.4 V), Green (+0.4 V) and violet (+1.2 V). To increase the electrochromic colour contrast of PPy/DS and investigate a possible modulation in the colour change, Girotto and De Paoli added indigo carmine to the electrochemical synthesis solution [69]. Photoelectrochromism of PANI was performed using photoinduced electron transfer between $Ru(bpy)_3^{2+}$ and methyl viologen (MV²⁺) molecules [70]. A series of alkyl substituted and unsubstituted poly 3,4 alkylene dioxythiophenes were synthesized electrochemically using 3,4-alkylenedioxythiophene derivative monomers by Anil Kumar et al. [71]. They have studied optoelectrochemical experiments and revealed that the nature of the substitution on the polymers had little effect on the extent of conjugation of the backbone. Recently, the search for polymers for electrochromic windows, combining attractive optical properties with stability, is advanced with poly(3,4-ethylene dioxy thiophene), PEDOT. The low bandgap allows the polymer to be almost transparent in the doped state and blue-black in the neutral state. The presence of some optical absorption in the range 1.6-2.0 eV causes a film of the doped polymer to have a light sky-blue appear-

Monomer Dopant	Dopant	Chromatic change		Voltage V (vs SCE)	
	Reduced state	Oxidised state			
Aniline	Cl ⁻	Yellow	Green	0 to 0.6	
Dimethylpyrrole	$\mathrm{BF_4}^-$	Green	Violet	-0.5 to $+0.5$	
Thiophene	ClO_4^-	Red	Blue	0 to 1.1	
Dimethylthiophene	BF_4	Light blue	Dark blue	0.5 to 1.5	
Dithienothiophene	ClO_4^-	Red	Black	0.4 to 0.8	

Chromatic changes and related voltage ranges associated with electrochemical doping processes for some selected conducting polymers

ance, for better transparency it would be desirable to suppress the band-gap by another 0.2 eV [72]. The colour of various electrochromic materials in the oxidised and reduced state is shown in Table 5.

Table 5

5.4.7.1. The solid-state electrochromic cell. A solid-state electrochromic cells similar to cells used for characterising conducting polymers before [73,74] was used for commercial purpose. The large area of laminated solidstate electrochromic devices were fabricated from polyaniline and solid polymer electrolytes, prepared by mixing protonic acids or alkali metal salts with either PEO or PEI and PAN based membrane. Such device switches rapidly from colourless to green between -3.0 to + 3.0 V and appears to be stable after several thousand switching cycles. The another solid-state electrochromic cell comprises one polymer (PEDOT) layer on a conducting ITO coated glass, one solid polymer electrolyte layer (poly(2-(2-methoxy ethoxy)-ethoxy) phosphazone, MEEP [75–77] or poly (oxymethylene-oligo(oxyethylene)) [75–81], doped with $LiClO_4$ and one ion storage layer (lithium intercalated vanadium oxide $Li_v VO_x$) [82]. The solid-state electrochromic cell is shown in Fig. 5a. The $Li_v VO_x$ layer has a very high coulombic capacity, almost 10 times higher than that of conjugated polymer [73].

The solid-state electrochemical cell [83] consisting of $\text{Li}_y \text{VO}_x$, amorphous PEO electrolyte and the electrically conducting polymer (poly 3,4 ethylene dioxy thiophene) works as an electrochromic device; and can be switched between opaque blue/purple and transparent sky blue which are very reasonable colours for a smart window or an electrochromic display and the required applied voltage is small (+1.5 V). The switching time at room temperature, from fully coloured to fully bleached, is about 4 s and the stability upon repeated switching is very good. Cyclic voltammogram for a solid-state electrochemical cell of PEDOT (PSS⁻)/POMOE-400(LiCIO₄)/Li_yVO_x is shown in Fig. 5b.

5.4.8. Electroluminescent display devices

Semiconducting conjugated polymers have been successfully used as the active materials in field-effect transistors, LED, polymer grid triodes and sensors [84–95]. Eversince the first discovery of electroluminescence (EL) in semiconducting conjugated polymers, interest has grown rapidly and many polymers have been successfully used in LEDs. The polymer based LEDs are especially attractive for use in display technology and the list of electroluminescent materials for producing various colours is presented in Table 6.

The great interest in such polymer based devices is understandable in terms of significant advantages that these systems have in possessing better mechanical properties and geometry possibilities as compared to conventional semiconductors [96,97]. Another favourable aspect of the polymer LED is that it is possible to cover the spectral range from blue to near infrared, even within a single family of conductive polymers such as polythiophene [98]. The recent demonstration of voltage-controlled electroluminescence colours from polymer blends in LEDs [98] as well as the possibility of obtaining polarised light from oriented polymers in LED devices extend the possibilities of fabricating 'exotic' polymer devices.

Polymer LEDs are constructed by sandwiching a layer of conjugated polymer (Fig. 6) between a pair of electrodes.



Fig. 5. (a) The solid-state electrochromic cell; (b) cyclic voltammogram for a solid-state electrochromic cell [83].

Colour of the emission light	Luminescent material
Red	Cyano-derivative of PPV, POPT
<i>(ellow)</i>	Poly(2,5-bis(cholestanoxy)-1,4 phenylene vinylene and poly(3-cyclohexane thiophene) (PCHT)
Drange	MEH-PPV
Green	Poly(p-phenylene vinylene) (PPV)
Blue	Poly(3,4 ethyelene-dioxy thiophene) (PEDOT), Poly(3-methyl-4,cyclo-hexane thiophene) (PCHMT)





Fig. 6. Simple construction of organic electroluminescent device.

Electrons are injected from cathode (aluminium, calcium and indium) and holes are injected from the anode (ITO). The mechanism for electroluminescence is also somewhat different from that found in conventional devices. When holes and electrons are injected into the polymer, they form positively and negatively charged polaron that can migrate under an applied field and radiatively recombine when they meet [99] yielding electroluminescence.

One of the advantages with polymer LEDs is the possibility to choose size and geometry freely. So far, this has mainly been exploited in making large (several square centimeters) LEDs. Granstrom and Inganas have shown that it is possible to go in the other direction and make the light source very much small if the micrometer and nanometer sized polymeric LEDs are fabricated. The two conducting polymers are used in EL devices as shown in Fig. 7. In gold coated glass, PEDOT is deposited as a hole injecting electrode and PTOPT is deposited on PEDOT as an electroluminescent polymer and Al/Ca is vacuum deposited as an electron injecting electrode [100-103]. The two conducting polymers are used in electroluminescence devices and the typical current as well as light curves as a function of applied voltage are shown in Figs. 8 and 9 for micrometer and nanometer sized diodes, respectively. Two different conjugated polymers have been used in making these small LEDs. The first one poly(3,4-ethylene dioxy thiophene) [100-103] (PEDOT) was used as the hole injecting contact; the other poly(3-(4-octyl phenyl) 2,2'-bithiophene) (PTOPT) was used as the electroluminescent layer.

Electroluminescence from substituted polythiophene polymer covers the full visible spectrum, from the blue into the near infra-red. The substituted polythiophenes have



Fig. 7. Schematic representation of the two conducting polymers used in LED.



Fig. 8. Current (solid line) and light (dashed line) curves as functions of applied voltage for $10\,\mu\text{m}$ diodes. The light is measured as the current from the photodiode [103]

all been designed to give varying degrees of main chain planarity. In this way, the conjugation length and band gap are controlled in a systematic manner [104]. Inganas et al. [105] extended the family of substituents to include alkyl– alkyl, cyclo-alkyl and alkyl–phenylene group. These four different polythiophene derivatives with band gaps varying by 2.0 eV display electroluminescence from blue into the infrared. Electroluminescence spectra of the above different polythiophene shown in Fig. 10. It is possible to achieve a colour spectrum in the whole visible region simply by substituting an appropriate functional group in a luminescent polymer. For example, moieties like pyrazoloquinoline (PAQ) and bispyrazolopyridone (PAPI) derivatives have been incorporated in luminescent polymeric system to get



Fig. 9. Current (solid line) and light (dashed line) curves as a function of applied voltage for 100 nm diodes [100].



Fig. 10. Electroluminescence spectra of PCHMT, PCHT, PTOPT and POPT [105].

full visible spectrum. A single layer device consisting of a poly(N-vinyl carbozole) host which was previously doped with PAQ_4 is explained by the domination of the dopant polymer interaction [106]. A scanning tunneling microscope was used to generate EL from the films of the conjugated polymer namely, poly(1,3-phenylene vinylene-co-2,5-dioctyloxy-1,4-phenylene vinylene). This allowed the spatial distribution of EL to be mapped across the film and also measurements of local EL emission spectra to be recorded [107]. Sensitivity of polythiophene planar LEDs to oxygen was observed by Kaminorz et al. [108].

For colour flat panel displays, organic semiconductors appear to be very promising. A novel means is described for the realisation of red, green and blue (RGB) dots based on an all organic colour transformation technique [109]. Report is also available on green LED using poly(1,4 phenylene

vinylene) (PPV) as an emitting layer [89,110] which has been prepared through a thermal elimination process from a water [111] or organic-soluble precursor polymer [112-114]. Several organic solvent soluble PPV derivatives have been developed in order to improve processability [115-117]. Zhang et al. [117] reported the improved quantum efficiency in green polymer light-emitting diodes with a silyl-substituted soluble PPV derivative. Poly(2-chloestanoxy-5-hexyl silyl-1,4-phenylene vinylene) (CS-PPV) showed high quantum efficiency with an air-stable aluminium electrode by adding an electron transporting molecular dopant, 2-(4-diphenyl)-5-(-4-tert-butyl phenyl)-1,3,4, oxadiazole (PBD) [118,119]. Silvl-substituted solvent processable poly(1,4-phenylene vinylene) (PPV) derivative, poly(2 dimethyloctyl silyl-1,4, phenylene vinylene) (DMOS-PPV) is synthesized by the dehydrohalogenation route from 2-dimethyl octyl silyl-1,4-bis (bromomethyl) benzene [120-122] and the light emitting properties of the polymer are in single layer electroluminescent devices (ITO/Polymer/Ca or Al) exhibit an emission maximum at 520 nm. The photoluminescence (PL) and EL spectra are shown in the Fig. 11 of the DMOS-PPV film with internal quantum efficiency in the range 0.2-0.3%.

5.4.8.1. Light emitting electrochemical cell (LEC). The invention of a new type of light-emitting device has been reported [123,124]. The LEC combines the novel electrochemical properties of conjugated polymers with the ionic conductivity of polymer electrolytes. In these solid-state LECs, the conjugated polymers are p-doped on the anode side and n-doped on the cathode side and a light emitting p-n junction is formed between the p-doped and n-doped regions. Heeger and coworkers [125] described the electrochemical operating mechanism of LECs and addressed the fundamental issues associated with the reversible formation of the light emitting p-n junction and used poly(1,4 phenylene vinylene), (PPV), admixed with a polymer electrolyte as the electrochemically active layer. A schematic representation of the mechanism of LEC is shown in Fig. 12.

5.4.9. Laser materials

For optically pumped lasers, conjugated polymers are used as their active material in solution and in thin films. There is now great deal of interest in the prospects of producing similar electrically pumped laser diodes. Laser emission has been observed from poly(2-methoxy-5-(2'-ethyl hexyloxy) 1,4-phenylene vinylene (MEH-PPV) in dilute solution in an appropriate solvent in direct analogy with conversional dye lasers [126]. An optically pumped polymer laser was recently demonstrated in which the gain material was a dilute blend of MEH-PPV (<1%) in polystyrene [127]. These thick (~100 μ m) films contain a dispersion of TiO₂ nanoparticles that combine the emitted photons by multiple scattering so that the distance travelled in the medium exceeds the gain length.



Fig. 11. Photoluminescence and electroluminescence spectra of DMOS-PPV [122].



Fig. 12. Schematic representation of the mechanism of light emitting electrochemical cells.

Luminescent conjugated polymers are shown to have gain narrowing as neat films of submicrometer thickness, including polymers with the backbone molecular structures of PPV, PPP and polyfluorene. Light emission was typically collected from the face of the sample, but lasing could be detected in all directions.

5.4.10. Solid-state rechargeable batteries

One of the most important energy storage applications of conducting polymer film is their use as cathode material for rechargeable battery in view reversible doping. Certainly, the concept of polymer batteries is very attractive in terms of the various interesting applications that such a electrochemical power source could offer. Polyaniline is stable in air and has high conductivity at ambient temperature. Polyaniline is one of the most promising candidates for electrochemical devices like light weight batteries, capacitors and electrochromic displays etc. [128–131].

A conducting polymer battery system having a configuration of a drycell (Leclanche) type, which can be recharged with a cyclability of 100 cycles would be preferred choice. The redox properties of conducting polymers have been utilized in charge storage device such as supercapacitors and batteries.

First, although most classes of conducting polymers can be switched between electrically neutral state as an oxidised (p-doped) state, very few polymers can be electrochemically reduced (n-doped). The coupling of a cathode and an anode based on the same polymer in the neutral and the p-doped states results in a very small cell potential and consequently conducting polymers that can only be p-doped are limited for use as cathodes in battery system.

The Leclanche cell is irreversible and therefore incapable of recharging because of the occurrence of side reactions. The e.m.f. of above system is above 1.6 V but the cathode potential is a function of pH. This value falls rapidly on continuously discharge whereas in secondary cells, such as lead accumulators (lead acid battery) whose electrode processes are almost reversible and the cell is based upon preelectrolysis of an aqueous solution of sulphuric acid saturated with lead sulphate between lead electrodes.

But assembly of polyaniline based dry cell battery is advantageous over the above said batteries due to its following market potentialities.

- Low cost, avoidance of explosive hazards, solid electrolyte, high-energy density, high-power density and saves space and volume.
- Rechargeable, less weight, pollution free, eliminating MnO₂ and leakage proof etc.
- Commercial purposes like button cells in wrist watches and AA (cylindrical cell type) used in wall clocks, transistors, camera etc.

 >100 cycles and lower cost than Ni-Cd battery and applicable in solar rechargeable battery.

Trivedi group have fabricated a dry cell using Polyaniline [132]. Fabrication of a dry cell using polyaniline is very simple and replaced MnO_2 from a dry cell (Leclanche) by chemically synthesised polyaniline. The configuration of the battery (Fig. 13) is Zn/solid polymer electrolyte/PANI.

The proposed discharge reactions of this battery are shown in Fig. 14. This battery uses solid polymer electrolyte composed of methoxy cellulose and polyvinyl sulfate with a cellulose sheet as a separator. The weight reduction from a conventional dry cell around 25% with open circuit voltage (OCV) 1.3 V and short circuit current (I_{sc}) as good as that of a MnO₂ based dry cell. This dry battery has been tested from repeated charge–discharge cycles and can be cycled for 50 cycles, with a cut-off voltages of 0.6 V.

Another system of rechargeable conducting polymer batteries consist of polyaniline as an anode and Li–Al alloy as a cathode and LiBF₄ in a mixture of propylene carbonate and 1,2-dimethoxy ethane as an electrolyte [133].

During charge–discharge, there is a large change in volume of polyaniline to cause inhomogeneous dimensional changes. However, these mechanical changes have been minimised by restricting depth discharges to 30% and incorporating solar charges in devices to continuously recharge batteries. The OCV is 3.0 V and energy density is 440 W h kg⁻¹.

5.4.11. Electrochemical supercapacitors

The 'supercapacitor' is a high-tech device that promises to supercharge the electronic products of the future. Capa-



Fig. 13. Configuration of the conducting polymer solid-state rechargeable battery [132].

The proposed discharge reactions are

at the anode and



at the cathode , giving the overall reaction





Fig. 14. The proposed conducting polymer solid-state rechargeable battery discharge reactions [132].

citor is a small device that stores electrical energy, when an electric field is applied across a dielectric, (the common double layer capacitor model is shown in Fig. 15) whereas batteries store chemical energy in the form of reactants which locally and externally release Gibbs free energy in the form of an electrical current. The electrochemical capacitors make use of a charged double layer formed at the electrode/ electrolyte interface and hence the capacitance depends upon area of the electrode. In an ideal capacitor, the amount of charge stored is proportional to the potential difference. The redox capacitor is based on the faradaic pseudo-capacitance of two-dimensional or quasi two-dimensional material at or within which redox process occurs. The second type involves reactions like oxidation/reduction in microporous transition metal hydrous oxide, RuO₂ [134], IrO₂ [135] and oxidation/reduction reactions of conjugated polymers [136,137]. These supercapacitors are expected to work in conjunction with batteries in electrical vehicles to provide necessary peak power performance and possibly to reduce



Fig. 15. The common double layer capacitor model.

the size and enhance the life expectancy of the battery. The use of a double layer capacitance in the ideal polarisation region of electrodes for a preparation of supercapacitors is well known. Cells with carbon black and carbon cloth electrodes are the most extensively studied. Recently, several papers were published that confirm the fact of accumulation of considerable charges in a system consisting of a current collector, conducting polymer and an aqueous or non-aqueous electrolyte. Use of conducting polymers instead of or together with carbon containing materials as supercapacitor components seems very tempting due to their high corrosion resistance, low temperature coefficient of resistance and wide technological possibilities for choosing an electrode formation method. Thus, Genies et al. [138] have reported charge density of 450 C g⁻¹ for polyaniline in a propylene carbonate LiClO₄ system whereas Gottesfield et al. [139] claim a capacity of 800 C cm⁻³ under aqueous acidic conditions. Kogan et al. [140] tested a laboratory prototype (Fig. 16) supercapacitor based on polyaniline electrodes and sulfuric acid electrolyte. They carried out experiments by using a capacitor cell, which comprised two polymeric electrodes with current collectors and separator wetted with electrolyte.

The inspiring observations by Calberg and Inganas [141] revealed the properties of poly(3,4-ethylene dioxy thiophene), PEDOT as the electrode material in an electrochemical capacitor. They inferred that PEDOT is an attractive material for use as an electrode material in electrochemical supercapacitors due to its fast kinetics and good electrochemical stability. The supercapacitors studies comprising two PEDOT electrodes and a liquid electrolyte (LiClO₄ dissolved in acetonitrile) and not optimised. Investigations for a PEDOT capacitor with a solid polymer electrolyte are under way [141]. It would be interesting to replace or coat one PEDOT electrochemical properties to increase the cell voltage of the device and increase the energy density.

Table 7 Commercial products based on conducting polymers

Conducting polymer	Applications	Commercial company	
Polyacetylene	Photovolatics	IBM	
Polypyrrole/silicon	Electronic devices	MIT	
Conducting polymers	Electrophotography	Kodak, IBM	
Polyacetylene/polypyrrole	Rechargeable battery	Allied signal, BASF, Seiko	
Polypyrrole	Molecular transistor, sensor	MIT, Abtech Sci. Inc. Yardley, PA	
Polythiophene, polyaniline	Optical display devices	Research & Development	



Fig. 16. Laboratory prototype supercapacitor based on polyaniline (1) case; (2) insulator; (3) current collector; (4) polyaniline electrode; (5) membrane; (6) rubber gasket [140].

6. Summary and outlook

The electrochemical synthesis of novel electronic materials and their structure showed that besides the application oriented development and optimisation, novel applications in more speculative fields such as polymer electronics or even molecular electronics may become feasible.

Thus, applications of conducting polymers as photoconducting devices, solar energy conversion (PV) cells, in polymeric coloured LEDs that could display images and form flat plastic screens for computers or TVs. They could also replace traditional LCDs, which are limited to a small size. Solid-state electrochromic cells for large area electrochromic devices (ECDs) are being used for commercial sign boards, time tables in airports and railway stations, calculators, clocks etc. In future, the world wide needs of economic fuel and pollution free environment can be met through the energy storage applications like rechargeable batteries and super-capacitors using conducting polymers as electrode material. These high-tech devices will be supercharge electronic products of the future. Some of the commercial products of conducting polymers are presented in Table 7. World wide several companies are racing to develop ultra-capacitors with millions of times the energystorage capacity of traditional capacitors. Ultra-capacitors store and release energy like batteries, but have vastly longer lives. They can unload their energy 10 to 100 times faster than batteries. The new devices may lead to electric vehicles exhibiting superior performance of sports cars by releasing bursts of power when accelerating or climbing. Ultracapacitors are of great use in cellular phones and supercomputers.

Most of the conducting polymers that have reached the actual application stage seem to be in a production test phase and are still waiting for a greater acceptance and utilisation on the current market. Therefore, it is quite unclear at the moment how much profit is really made with devices based on conducting polymers and whether the world wide sales figure of synthetic metals which was forecast as 1 billion US\$ in the year 2000 [142] will be reached.

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