

CONDUCTING POLYMER BATTERIES — AN ASSESSMENT

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The use of conducting polymer electrodes in the fabrication of rechargeable batteries has been discussed from the origin of its use to the present state of the art. The principle behind its use, the mechanism and the basis of cell fabrications based on different types of conducting polymer systems are explained. Also emphasis on the importance of modification of polymer matrix and complete evaluation of their characteristics have been made with a view to optimise a commercially viable conducting polymer battery.

Key words: Polymer batteries, polyaniline, polyacetylene, polythiophene, polyphenylene, heterocyclic compounds

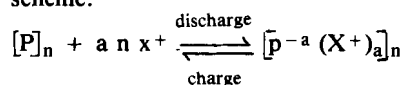
INTRODUCTION

Polymeric materials with the emergence of their electrical functionality [1] coupled with their physical and chemical properties such as high strength-to-weight ratios, toughness, low cost, molecular tailoring for desired properties and ease of processing into different shapes have become competitive materials in diversified electrochemical applications. These materials are known as "conducting polymers" where majority of them are extrinsically conducting systems. The electrical conductivity can be imparted to polymer systems possessing conjugated double bond and the process is referred to as doping. This type of doping can be correlated to conventional oxidation and reduction process [2] which respectively yields p-type and n-type conducting polymer systems. Thus conducting polymers can be synthesised [3] as "metal", or as p-type or n-type semiconductors through (i) simple chemical doping (ii) photochemical doping or (iii) electrochemical doping. Of all these types of doping, electrochemical methods provide a more efficient and economical procedure which offers a doped polymer product with a consistent and uniform preselected room temperature electrical conductivity. Because of this unique advantage, they find applications (a) as electroactive materials in the fabrication of light weight rechargeable secondary batteries [4] (b) as semiconductor or "synthetic metal" in the fabrication of a solar cell [5] (c) as electrodes in the electrosynthesis [6] (d) as modified electrode [7] or (e) in electrochromic devices [8]. Although the use of these materials in the above areas of applications has been successfully demonstrated, their use as electroactive materials in the fabrication of light weight rechargeable batteries has been more attractive, and constant efforts are being made towards the possible commercial exploitation of these systems. Hence, the present report analyses the various possibilities of fabricating a battery out of different types of conducting polymers and correlates the influence of the characteristics of the system under consideration with its performance, with a view of optimising the cell configuration.

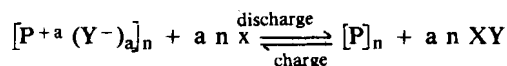
Principle of the conducting polymer battery

This stems from the process of electrochemical doping of conducting polymer systems wherein p-type material is obtained by the migration of anionic dopant ions into anode active polymers and n-type material is produced by the migration of cationic

dopants into the cathode active polymer. These electrochemical reactions are reversible i.e. p-type doped polymers are electrochemically reducible and n-type doped polymers are electrochemically oxidizable. This particular phenomenon of electrochemical doping and undoping is identical to charging and discharging reaction of a given voltaic cell, and this forms the basis for the construction of a rechargeable secondary battery out of conducting polymers. It can be represented in the following reaction scheme:



'P' stands for the repeat unit of the polymer, 'a' is the doping level 'X' refers to cation used, and 'n' number of repeating units. This is same as electrochemical 'n-type' doping and undoping.



This corresponds to an electrochemical undoping of p-type doped polymer and redoping thereafter.

Selection and basis of conducting polymer anodes and cathodes

Novel secondary batteries can be fabricated by employing a conjugated polymer either in dopable or doped form as the electrode active material of one or both of their electrodes and various electrochemical doping and undoping reactions can be used as charging and discharging processes. The electrolyte component of such secondary battery comprises of a compound which is ionizable into one or more ionic dopant species suitable for effecting the appropriate electrochemical doping. The batteries can be assembled initially either in charged state or uncharged state, the latter requiring in situ conversion to charged state through the process of electrochemical doping. Thus a wide variety of novel secondary battery systems can be constructed. Broadly three classes are available and the following are their basis.

Class I

In this class, the anode of the secondary battery in its charged state includes as its anode active material an n-type conducting polymer. This includes a wide variety of battery systems wherein such anode is employed in combination with various compatible electrolytes and cathodes. The discharging mechanism of such secondary battery involves the electrochemical undoping of the cation-doped

conjugated polymer anode, the cationic dopant species being retrievably released from the polymer into the electrolyte system. In the uncharged or discharged state of such secondary battery, its anode active material is the polymer in the undoped form. The discharging mechanism of such secondary battery involves the electrochemical doping of such cation-dopable polymer.

ex: ClO_4^- doped p-type $(\text{CH})_x$ can be coupled as cathode active material to Li anode.

Class II

In this class, the cathode of the secondary battery in its charged state includes as its cathode active material, a p-type conducting polymer. This class also includes a wide variety of systems wherein such cathode is employed in combination with various compatible electrolytes and anodes. The anodes can be of metals that are used in conventional battery systems. The discharging mechanism in this class is same as in Class I with anionic dopant species being retrievably released from the polymer into the electrolyte system. In the discharged state, the cathode active polymer remains undoped and charging can be done through electrochemical p-type doping as is practised in Class I.

ex: Li doped n-type $(\text{CH})_x$ as anode along with TiS_2 as cathode

Class III

In this configuration, a secondary battery in its charged state includes n-type conducting polymer as anode-active material and p-type anion doped polymer as its cathode active material. The discharging mechanism of such secondary battery involves simultaneous electrochemical undoping wherein the cationic and anionic dopant species being retrievably released from their respective host polymers into the electrolyte system. The charging mechanism involves the simultaneous electrochemical doping into respective n-type and p-type conducting polymer system.

ex: Li doped n-type $(\text{CH})_x$ as anode along with ClO_4^- doped p-type $(\text{CH})_x$ as cathode.

The above classifications give rise to a number of combinations of conducting polymers either as both electrodes or one electrode in combination with other conventional systems. All the possible systems are under active consideration and a thorough analysis decides the utility of polymer electrodes.

Characteristics of conducting polymer batteries

All the potential conducting polymers have been examined as electroactive materials in the construction of a secondary battery, and the influence of doping level, the characteristic nature of the polymer, and their surface morphology play a vital role in deciding the performance of the cell so constructed. The following individual systems illustrate the progress that has been made so far towards a possible technological development.

Polyacetylene batteries

Of all the polymers so far reported, polyacetylene has received maximum attention and has been widely exploited as a possible

electrode in the battery. It has been used both as anode active material as well as a cathode active material. Also, it has served as useful electrode in combination with conventional metals used in the traditional batteries.

A cell constructed with polyacetylene as both electrodes has offered excellent battery performance. The configuration n- $(\text{CH})_x$ - LiClO_4 + propylene carbonate / p- $(\text{CH})_x$ exhibits [9] an open circuit voltage of 3.5V and a short circuit current of 28mA/cm². Experimental energy density has been 424 Wh/kg. It possesses 2000 successive charge/discharge cycles and is found to be useful in the temperature range from -20°C to 50°C . This is one of the attractive examples among the systems hitherto reported and this particular configuration claims light weight, high power and high energy density batteries, besides being portable. The polyacetylene used in the cell possesses the best surface characteristics as is evident from the fact that the migration of Li ions in the film becomes smooth due to an interwoven network of $(\text{CH})_x$ fibrils, and the precipitation of Li on the cathode electrode is prevented. Long term cycling in this type of configuration has been achieved because of the use of dehydrated LiClO_4 , propylene carbonate and dried polyacetylene electrode.

Another cell of the type $|\text{CH}(\text{ClO}_4)_y|_x/\text{LiClO}_4/\text{Li}$ is also found [10] to be quite effective in delivering useful power density (30 kw/kg) and energy density 255 Wh/kg. The success behind such larger outputs of power and energy density is due to the nature of film which consists of fibrils $\sim 200\text{\AA}$ in diameter. This permits close vicinity to electrolyte, thus offering good accessibility of counter ions, e.g. ClO_4^- . This coupled with larger surface area accounts for the higher output. Thus the preparation of polyacetylene film with well defined surface morphology is a vital factor and is further demonstrated by the fact that polyacetylene films possessing fibrous, highly stretched and porous structure exhibit different performance in a battery assembly [11,12]. These facts clearly stress the importance of surface characteristics of polyacetylene film which can easily be governed through different synthetic recipes.

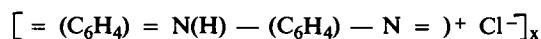
Polyacetylene has also been examined as a useful electrode with titanium disulfide, TiS_2 [12, 13] and appreciable performance leading to an energy density of 108 Wh/kg.

In such configurations, the influence of doping level over the performance has also been assessed, and it is found that different characteristics are obtained based on different doping levels [14]. There are many reports evaluating polyacetylene as electrode active material in the assembly of cells which illustrate polyacetylene as a potential candidate for assembling a viable battery [15-23]. The importance of doping level, surface morphology and nature of counter ion are so vital, and a careful choice coupled with the necessary ingredients is bound to enhance the performance of polyacetylene batteries. In addition, the relationship between the structure of doped polyacetylenes and their electrochemical behaviour must be understood to achieve better capacity than that obtained now. It is worth to remember that polyacetylene electrodes behave better only in rigid atmosphere and lose their electrochemical sensitivity in air. This has to be nursed, and efforts are under way to enhance the stability of these electrodes either through careful

choice of counter ions or through modification of polyacetylene matrix in the conventional manner. There are successful attempts of preparing polyacetylene whose stability in air is appreciable, but their use as effective electroactive material is yet to be assessed.

Polyaniline batteries

Polyaniline is another interesting conducting polymer and has received considerable attention towards the development of suitable battery. Unlike polyacetylene, it is stable against air and moisture. Various ill-characterised forms of polyaniline are possible through oxidation of aniline. The one which has good electrochemical sensitivity is a benzenoid - quinonoid diiminium salt having the composition as follows.



This form can conveniently be synthesised both through chemical and electrochemical routes.

Cells have been fabricated and evaluated based on polyaniline electrodes in conjunction with metal electrodes employed in conventional batteries. The first reported [24] polyaniline based cell yields a capacity of 13 Ah/kg. The most sensible and useful are the systems examined with zinc and lithium electrodes. A Zn/ZnSO₄/polyaniline configuration has been studied by two different groups [25,26] and the maximum that is obtainable is 108Ah/kg and energy density of 111 Wh/kg with the coulombic efficiency of 100% over 2000 charge/discharge cycles. This is indeed one of the best performances of polyaniline battery. Also a cell based on polyaniline/H₂SO₄/PbO₂ has been found fruitful and offers appreciable performance. A Li/LiClO₄ in propylene carbonate/polyaniline based battery [27] yields an energy density of 539 Wh/kg, with an average discharge voltage of 3.65 V. Thus both aqueous [28] and nonaqueous [29] batteries are possible based on polyaniline. The use of polyaniline as cathode in conjunction with Zn-Hg anode, in authors' laboratory, yields [30] an open circuit voltage of 1.4V and coulombic efficiency for each complete cycle remained within the range of 93-95%. Polyaniline has also been examined as anode active material with Li doped aluminium [31,32] as cathode. A completely packed battery [33] based on polyaniline with Li - Al alloy is now available, specifically meant for memory back up of power source of SRAM or working resources of LCD. This packaged coin type cell offers a working voltage of 3.3 - 2.0 V with life cycles more than 2000 offering normal capacity of 4MAH, besides being usable in the temperature range — 20°C to 60°C.

Active interests are being shown in polyaniline-based battery systems, as it enjoys better stability in air. Appreciable performance of these cells make cells of this type more attractive.

Poly (p-phenylene) batteries

Polyphenylene in another class of material requiring more attention because of its high stability and processability of the polymers. Poly p-phenylene has been examined both as anode and cathode and also in conjunction with the traditional metals. In all the configurations, it has offered useful performance. When Li is used,

it displays [34] an open circuit voltage of 4.4 V which is higher than the polyacetylene/Li battery. This is due to the higher ionization potential (5.6 eV) for the undoped poly p-phenylene than the polyacetylene (4.7 eV). The evaluation of this particular polymer needs more careful analysis to optimize the best possible power density and energy density. The major disadvantage presently encountered [35] with this system is that it shows poor stability in conventional nonaqueous solvents used in cell fabrication such as propylene carbonate. The search for other useful solvents may overcome this difficulty. The attraction of this material lies in its high structural integrity, high voltage, high insolubility and high ionic mobility.

Heterocyclic polymer batteries

In this class, polypyrrole and polythiophene are better demonstrated conducting polymer systems than others. However their assessment as electroactive material in the fabrication of cells are of recent origin and are receiving constant attention now to a larger extent. The main attraction of this class of polymers is their stability in air. Besides, they can easily be synthesised without any elaborate arrangement as is required for polyacetylene, thus becoming a competitive material to it. The electrochemical reversibility, particularly for polythiophene [36], is as good as polyacetylene, and enjoys better edge over poly p-phenylene and poly p-phenylene sulphide. Besides, there is a possibility of introducing a variety of counter ions into the polymer matrix, an obvious advantage of the electrochemical route over chemical route, and consequently conducting polymers exhibiting different electrochemical behaviour are possible. Such materials offer wide variety of electrodes for the possible use in the construction of a cell.

A polypyrrole-based battery with Li-Al alloy offers [37] a capacity of 130 Ah/kg and this particular combination is the best demonstrated pair.

Polythiophene is another interesting electroactive material under active consideration as both anode and cathode of a cell. An all-polythiophene cell [38] offers an open circuit voltage of 2.8V and a short circuit current of 5mA/cm² in a nonaqueous environment. A polythiophene-based battery in conjunction with Li [39] offers a power density of 2.5 x 10⁴ W/kg and an energy density of 140 Wh/kg. The authors' experience with an assembly of battery based on this polymer shows [40] that it is possible to assemble a primary as well as a secondary battery. This particular polymer with better electrochemical behaviour in different environment [41] is expected to be a useful electroactive material in the battery application. The evaluation of such polymer electrodes presently receives consistent attention, and a thorough understanding of their behaviour in combination with the traditional metallic electrodes and also their counter electrode is bound to lead to a useful system. The unique advantage of this class of polymers is the stability at room temperature and the number of doped polymers that are available for different combinations.

Besides, poly diethiophene has been proved to be another effective electroactive material in the fabrication of a rechargeable secondary battery [42,43] and a cell consisting of such electrodes yields a capacity of 54 Ah/kg with ClO₄⁻ dopant offering better

cyclability with no evidence of appreciable degradation and an apparent stability to oxygen.

On the whole, heterocyclic conducting polymer systems are advantageous and require further studies especially in relation to surface characteristics, flexibility and mechanical stability.

Future scope

As is seen in the preceding sections, a handful of conducting polymers serve as potential and revolutionary electroactive materials. Majority of the cells so far constructed are in nonaqueous medium, and batteries in aqueous systems need to be developed to enhance higher rates of operation and safety handling. Since the charge density of a conducting polymer battery is a function of doping level, the useful doping profile of the given conducting polymer is to be optimised for achieving best possible characteristics. Further, this also suggests the possibility of fabricating a cell to the desired power and energy output, if the demand is so specific. Surface morphology of the conducting polymer is so crucial, and a thorough understanding of surface characteristics of each system needs careful analysis to assess their electroactive character. Another important point to be nursed is the enhancement of the stability of polymer electrode, especially in the case of polyacetylene. Besides, processability, flexibility, adherence to substrate and porosity are to be tailored for all the materials so far known which require modification of polymer matrix through traditional polymer processing. There are encouraging established routes to achieve this requirement without sacrificing the basic character of conducting polymer systems.

Polymer offers versatility of design which is not possible with metals or inorganic powers. In particular, thin films can easily be made and shaped to fit the appropriate devices. If processable and mechanically stable polymer electrode is achieved, it is expected to remove a metallic current collector that is presently used in these systems. This will indeed make the battery light weight and if achieved, will generate more impact in streamlining the battery user industries. As far as cost is concerned, except for polyaniline, others stand less competitive. However, if the quality is the only criterion, these conducting polymer batteries may meet some specific requirements as systems of varying performances are possible. With substantial progress so far made in these batteries, it can be predicted that these may address commercially special uses in the electronic market, as evident from a miniature battery already developed [23]

CONCLUSIONS

Thus the idea of using conducting polymer electrodes in the battery components is certainly of great importance and this justifies the continuously growing interest in this novel type of batteries. Larger research efforts devoted to the electrochemical characteristics of these systems, may result in an effective battery with better cyclability and stability. It appears that the prospects of developing a suitable conducting polymer battery (at least in the miniature shape) in a practical electrochemical environment looks encouraging and lucrative.

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