

NON-METALLIC METAL-LITHIUM CELLS

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ABSTRACT

Organic polymer-based lithium cells are compact, stable during cycling, free from corrosion problems, and leak-proof and do not change the shape of the electrode even after several cycling. This review details some of the emerging class of organic polymers which are used in the battery area.

Polyethylene oxide and polyacetylene secondary solid-state battery will be suitable for many electronic gadgets.

INTRODUCTION

Portable power sources are increasingly used in many electronic gadgets. With the advent of the miniaturised electronic gadgets like wrist watches, calculators, hearing aids, flash cameras and video games, the power sources have to be miniaturised [1]. Many lithium cells were invented to cater to the needs of the miniaturised electronic gadgets. Invention of nonaqueous lithium cells of high voltage and long shelf life paved the way for miniaturised power sources [2]. Wafer-thin lithium cells are produced to accommodate them in miniaturised electronic gadgets. The quest for finding thinner cell with high energy density is the aim of scientists. Solid-state cells are the answer for the miniaturised cells. Unfortunately, conductivity of the solid-state electrolytes was a problem which hampered the progress of the solid-state cells. After the successful discovery of super-fast ions in solid-state materials impetus came in the solid-state work in batteries. This success resulted in the invention of solid-state batteries.

Solid-state materials : Materials for solid-state cells range from transitional group metal oxides [3] and chalcogenides, oxides of cadmium [4], copper [5], lead [6] and sulphides of copper [7], titanium [8], silver [9] and cadmium [10]. Many new materials can be considered for conductivity in solid-state batteries [11]. Some of the electrolytes which are considered for conductivity in solid-state materials are poly-phase solid electrolytes [12], (LiI-Al₂O₃, $2.4 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$). Noncrystalline electrolytes (glass-like materials (eg. beta alumina) [13], crystalline solid electrolytes (eg. LaF₃CaF₂) based on fluoride ion conductors [14, 15] and lithium ion conductors (Li₃N) [16], proton conductors (HOUPO₄ 4H₂O) [17] and polymeric solid electrolytes (polyethylene oxide (PEO) and polyacetylene (PA) with inclusion of lithium perchlorate) [18, 19]. Intercalated polymers have the property to charge and discharge several cycles. Thus, the organic polymers with poor conductivity can be made to behave like metals if their conductivity is between 10^{-7} and $10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ and it increases with temperature. Interest has been evoked to make use of this property for developing polymer-based batteries [20]. Solid-state batteries with lithium-organic polymers have commercial potentialities.

Solid-state batteries : Solid-state batteries [21] are compact, thin, wafer-like cells which operate at ambient temperatures. These cells are readily rechargeable [22]. Solid-state cells have long shelf life (more than 20 years) and are leak proof since no solution is used. These cells are fabricated with solid-electrolytes and therefore they are free from self discharge and corrosion properties. These cells can be conveniently stacked and at the same time the thin wafer structure of the cells is maintained. High energy density, light weight organic solid-state cells based on lithium metal have great potentialities.

Many organic polymeric compounds like polyethylene (PEO) oxide [23], polyacetylene (PA) [24], polyvinyl ether (PVE) [25], polyvinyl pyridine (PVP) [26] and blends of the above polymers are tried as cathodes for solid-state lithium cells [27]. These polymers show low conductivity of the order of $10^{-14} \text{ ohm}^{-1} \text{ cm}^{-1}$ [28]. Further, by doping the above polymers with suitable salts like (LiClO₄) [29], LiCF₃SO₃ [30], NaSCN [31], LiAsF₆ [32], NaClO₄ [33], LiSCN [34] and NaI [35], it is possible to get conducting polymers. Thus, by inserting a suitable ion in the above polymers, the nonmetallic property of the polymer can be changed. The insertion-electrode so obtained shows the property of reversibility [36-39]. In a suitable medium, this electrode can then be charged and discharged several times.

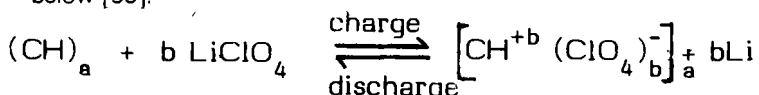
The doping procedure in a polymer is very simple. Insertion of the electrolyte in a polymer is made chemically [40], mechanically [41] or electrochemically [42]. In certain cases, doping can be achieved by interacting the polymer with the solvent and the electrolyte. Electrochemical doping can be made by passing current in a cell containing polymer electrode (as cathode) and platinum electrode (as anode) and a suitable electrolyte. In the process of doping, the electrode gets charged and in the reverse process, discharge takes place. The polymer electrode has normally a very large surface area [43]. Sometimes, the electrode area reaches a value of 50 m²/g. Lithium ion can be inserted into the electrode without changing the area of the surface. The change of shape of polymer electrode during the charging does not occur. The morphology of the polymer is fibrous in nature and its mechanical strength is found to be quite good. This property helps to shape the polymeric material to any desired configuration. A few polymer-based lithium cells are given below :

1. Lithium-polyacetylene cells [44] : Polyacetylene (CH)_n, is prepared by polymerising acetylene gas with catalyst [45]. This is perhaps the simplest conjugated polymer. This polymer can be doped with suitable dopants for controlling the electrical resistivity. The electrical resistance varies between $10^{12} \text{ ohm}^{-1} \text{ cm}^{-1}$ and $10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$, depending on the concentration of the dopant [46]. Polyacetylene exists in two forms, namely, the *cis* and *trans* isomers [47]. When the dopants are inserted in the polymer, it is observed that the *cis* isomer shows better conductivity than the *trans* isomer. The conduction of the polymer depends on the concentration of the dopants present in it and this value sometimes goes more than 10 times from its original value [48]. In the doped stage (CH)_n is believed to exist as a stable (CH⁺)_n carbonium ion.

Several methods are available to dope the organic polymer. In one of the methods, the following technique is employed :

Polyacetylene electrode is dipped in 0.3 M lithium perchlorate dissolved in PC. The other electrode is either platinum or nickel. After half an hour of electrolysis, the polymer electrode was removed for use [42]. In another method, doping was done conveniently using a vapour dopant [45]. Recently a simple technique was developed for doping polyacetylene [46]. In this technique polyacetylene is melted and then the dopant is added. The product is cooled and then dissolved in acetonitrile. The solution is carefully poured over a cleaned metal surface so as to form a thin film.

The mechanism of electrical doping has been explained in the following way [49]. Doping of polyacetylene results from charge transfer. The charge transfer occurs from polymer to acceptor (A) with polymer chain acting as a polycation, in the presence of a A⁻ species (in the case of iodine, the species is I₃⁻). For donor (D), the polymer chain acts as a polyanion in the presence of D⁺ species. This A⁻ or D⁺ ions reside between the polymer chain or the surface of the polymer fibre. The charge transfer need not be complete. The resulting electron, already on the polymer chain, is weakly bound to the D⁺ or A⁻ ions, thereby forming donor D⁻ or acceptor A⁻ states in the gap. The ability of the doping solution to reduce the polyacetylene chain is more for the cis than for the trans form [50]. Polyacetylene is analogous to inorganic semiconductors and on chemical doping, n-type or p-type semiconductor property can be noticed. Polyacetylene is crystalline in nature and its density is 0.4 g/cm³ [51, 52]. Polyacetylene (CH)_n, where n = 8 or more, has been recently used in secondary lithium cells. A cell can be constructed with doped polyacetylene and lithium metal. The principle of operation of the cell is given below [53].



A number of anions like BF₄⁻, SCN⁻, PF₆⁻, and I₃⁻ can be used in place of ClO₄⁻ ion. Served lithium cells based on polyacetylene are reported in literature.

A cell [54] was fabricated with (CH)_n as anode as well as cathode along with a binder and a separator. Here the reduced form of (CH)_n acts as a cathode and the oxidised form of the (CH)_n acts as anode. The cell is similar to the concentration cell. In another example [46], (CH)_n is used as one electrode and the other electrode is sodium. The cell EMF is 3.5 volts. The EMF of polyacetylene sodium cells is compared with lithium-titanium sulphide cell. A lithium polyacetylene secondary cell with improved discharge efficiency using polyacetylene of increased dopant concentration has been reported [55]. A secondary polyacetylene lithium cell maintaining a constant voltage even after 500 cycles of charge and discharge has also been reported [56]. Success of the cell lies in developing a stretched polyacetylene film, having a fiber structure and anisotropic conductivity of the order of 3.2 × 10⁻⁹ ohm⁻¹ cm⁻¹. The polymer was precipitated from triethyl aluminium using titanium tetrabutoxide catalyst. This film was coated with a titanium wire. Lithium was, of course, used as the anode. A very interesting method of fabrication of polyacetylene cell has been described [57]. Cathode and anode are made of a compact mixture containing polyacetylene, acetylene black or graphite powder and sodium polyacrylate binder. Lithium perchlorate dissolved in propylene carbonate or dimethoxyethane is used as the medium. A 900 micron thickness lithium-organic electrolyte battery of 3.05 volts has been reported in literature [58]. The cell consists of lithium anode and polyacetylene doped with I⁻ or AsF₆⁻ cathode and the electrolyte is calcium fluoride or magnesium fluoride.

2. Lithium/polyethylene oxide (PEO) : Polyethylene oxide is prepared from ethylene oxide [59, 60]. Ethylene oxide is a liquid whose boiling point is 12.5°C, which has a tendency to polymerise in the presence of catalysts like stannic chloride [61]. The polymerisation of ethylene oxide results in the formation of five types of polyethylenes of different molecular weight [62]. The molecular weight ranges from 4650 to 430440. Commercially ethylene oxide can be polymerised by passing its vapour through KOH or NaOH [63-65] and keeping the temperature in between 40 and 50°C. The degree of polymerisation of PEO depends on temperatures. Polymer electrolyte film of various composition with polyethylene oxide, and lithium trifluoromethyl sulphionate has been considered for fabricating lithium cells [66]. Polyethyleneoxide-lithium iodide mixture shows high conductivity even at low temperature [67]. A mixture of polyethyleneoxide-LiCF₃SO₃ exhibits conductivity of the order of 10⁻³ ohm⁻¹ cm⁻¹ [68]. The limiting current exhibited by the above mixture has been studied in detail [69].

Doping of polyethylene oxide is done in a simple way. LiCF₃SO₃ electrolyte is mixed with PEO and the mixture is then melted. The sample is then dissolved in acetonitrile and the solution carefully poured over a substrate. In this way, thin films of polyethylene oxide can be prepared.

An all solid-state polyethylene oxide-based lithium cell has been recently fabricated [66]. These authors have fabricated a cell in the following way. The cathode having a composition of V₆O₁₃ has been prepared by thermal decomposition of ammonium vanadate. The cell consists of V₆O₁₃ cathode, LiCF₃SO₃ electrolyte and lithium anode. This cell showed several cycles of discharge.

Recently a solid state battery with a configuration Li/Li₃N/LiCF₃SO₃ polyethylene oxide/TiS₂ cell was reported [70]. The cell was cycled at 120 to 170 cycles at 0.25 to 2 mA per sq.cm. The cathode is made of TiS₂. An all solid-state polymer based rechargeable lithium cell has been studied [71].

3. Other materials : In addition to polyethylene oxide and polyacetylene, other materials like polyvinyl pyridine [72], pyridine or quinoline groups with oligomeric and polymeric structures were considered [72]. Polyvinyl pyridine [73] has been also considered as a solid-state cathode for lithium batteries.

Polyphenylene [74], polyphenylvinylene [75] are also a class of compounds recently emerged as conducting polymers. Heterocyclic compounds recently emerged as conducting polymers. Heterocyclic compounds [76] like pyrrole, indole, azulene, thiophene and furan were studied recently.

Physico-chemical studies : Many physico-chemical techniques [28] are employed for understanding the phenomenon of conductivity, transport numbers and interfacial kinetics of intercalation compounds. Stereospecific regularity of the polymers are generally crystalline in nature [77] but the amorphous forms show nonstereoregularity [78]. The mechanism of transport in polymers were recently studied using the equation.

$$t = t_0 \exp \frac{C_1 (t+t_0)}{C_2 + (t+t_0)} \quad (1)$$

where C₁ and C₂ are given by C₁C₂ = B and

$$t = A \exp \frac{B}{(t+t_0)} \quad (2)$$

t₀ reduces to the transport parameter which is expressed by D^{1/2} σ t^{1/2} where D is the diffusion coefficient and t is the temperature of transition from amorphous or crystalline nature to glassy nature (t_g) σ is the conductivity and C₂ is given by (t_g+t).

Conductivity data and the Arrhenius activation energy calculations are particularly useful for phase transition studies in conducting polymers [79-80]. The wellknown log σ vs $1/T$ plot for various conducting polymers will indicate the nature of conductivity for different types of polymers. According to conductivity data the polymers are classified as Type I, Type II and Type III. Type I compounds do not show crystalline character. Type II compounds show Arrhenius conductivity below 350°K and obey Vogel-Tammn-Fulchner law as indicated in equation (2) and Type III compound helps us to understand the change in activation energies. The same polymer can be prepared in different solvents [81-83] and it is observed that the phenomenon of allotropies exist in them. The mechanical properties of the polymers which are important for battery work have been studied for polyethylene oxide (PEO), polypropylene oxide (PPO) and PEO-PPO copolymers with isocyanates [79, 84, 85]. Strengthening of the polymers with fillants has been studied [86] very recently to understand the stability of the polymer electrodes. Cyclic voltammetry studies [87-89] are particularly useful for estimating the stability of the battery electrodes. In a battery, reduction of metal ion takes place in the high electron activity centre and the insertion of metal ion occurs at the low activity centre of the polymer electrode. Also the reduction of the polymer network occurs at the high electron activity interphase and the oxidation process occurs in the low electron activity centre.

The kinetic reaction processes at the interphase have been studied with (a) symmetrical metal electrodes and (b) with polymer electrolytes and also unsymmetrical electrolytes i.e., Li-Li combination for (a) type metals and Li-Al alloy with TiS₂ combination for (b) type materials [90-92]. This study throws light on the precise information regarding the transfer impedance at the interphase. The phenomenon of dissolution and possible steric hindrance for cross linked polymers can be studied with impedance measurements [93]. The phenomenon of transport process has been studied carefully for understanding the process of intercalation. If the polymers show negligible resistance, it can be concluded that the transport processes are accompanied by high conductivity [94]. The mobilities of ions in a concentration cell are studied by e.m.f. measurements [95]. In intercalate d compound metal and its alloys are reversible to each other during the process of polarisation and it is possible to understand the nature of charge transfer and the diffusion process arising out of concentration gradients [96]. The limiting current can be calculated from the equation

$$i_{ll} = \frac{4RT}{nf} \frac{\sigma_+}{\delta} \quad (3)$$

where i_{ll} is the limiting current density, σ_+ is the cationic conductivity, δ the diffusion layer thickness. The time of depletion can be calculated from the diffusion equation which is given below.

$$t = \frac{C}{\delta RT} \left[\frac{i}{4RT\sigma_-} \right] \left[\frac{i}{i_{ll}} \partial F \right]^2 \dots (4)$$

where C is the concentration of depleting ion σ_- is the anionic conductivity and t is the time of depletion and i is the cell current. From the equation (4) it is clear that the anionic size should be as small as possible. Thus in a lithium solid-state or polymer based intercalated cell, it can be concluded that the anionic size should be small. Experimental studies were carried out with ClO₄⁻, CF₃SO₃⁻ ions for understanding the anionic effect [28]. Further studies were carried out with complex impedance spectroscopy [97, 81] and NMR spectroscopy for understanding the time of

depletion of ions [98]. Recently, NMR, ESR [100] and Mossbauer Spectrochemical methods [101] are used for understanding more about intercalation compounds.

Thus the conductivity, mobility and transport property, interfacial kinetics and cyclic voltammetry measurements help us to know the inner details regarding the physical characteristics of the polymer electrodes. The spectral instruments like IR, NMR, EPR, ESR, X-ray and other optical instruments are particularly useful to throw light on the concentration profiles and the nature of the linkages of the polymers and the insertion ions.

CONCLUSION

Considerable amount of interest has been evoked for research activity in molecular metals. These materials have wide applications in batteries [102], LED display devices [103] and photoenergy conversion devices [104]. The stability of the polymer is very important for selection to the above devices. Different types of polymers viz. thermosetting (soft and hard varieties) cross linked polymers (polyvinyl acetates and polyvinyl alkanes) and heterocyclic polymers (polypyridine, polyquinoline etc.) show different physical properties. These physical properties should be studied in detail for tapping its utility in various fields. The main work in the batteries based on molecular metals with lithium is to identify the suitable polymer. The cells produced with these macro-molecules should be stable during cycling. The cells produced with molecular metals are light in weight, and leak proof. Medium size cells are already produced with thin films.

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