Chapter 1

Introduction

1. INTRODUCTION

Recent research and development activities have been primarily aimed at the improvement of battery systems for several applications, ranging from cellular phones, cameras and other electronic devices to electric vehicles and space technologies. Indeed, the concept of power source capable of combining high energy density content with modulable, flexible structure is very appealing for the consumer electronic market [1]. This kind of modulable and flexible power source can be constructed with the help of polymeric electrolytes. Thus, our research is focused mainly on developing flexible polymer batteries for various applications with the help of PVDF as a host polymer. Usually, the polymers are insulators and they are deliberately made to conduct ions by doping salts. In the present study, the dopant is $LiBF_4$.

1.1 Electrochemical Power Sources or Batteries

Battery is not a commodity in itself. Batteries are part of a system where they can act as a power source. A battery is a device that converts the chemical energy contained in its active material directly into an electrical energy by means of an electrochemical reaction. Usually the term "battery" refers to a combination of cells joined in series, parallel and/or series and parallel. The basic electrochemical cell consists of three major components that are the anode, cathode and liquid electrolyte as shown in Fig. 1. 1 [2].

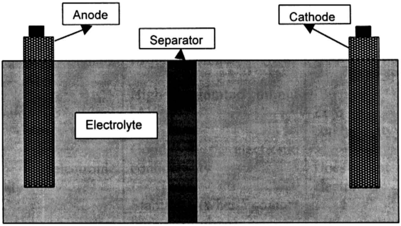


Fig. 1.1. Basic components of the electrochemical cell [2]

(i) The anode or negative electrode-the reducing or fuel electrode-which gives up electrons to the external circuit and is oxidized during the electrochemical reaction.

(ii) The cathode or positive electrode-the oxidizing electrode-which accepts electrons from the external circuit and is reduced during the electrochemical reaction.

(iii) Electrolyte-the ionic conductor-which provides the medium for the transfer of ions inside the cell between the anode and the cathode. The electrolyte is typically a liquid, such as water or other solvent, with dissolved salts, acids or alkalis to impart ionic conductivity.

The most advantageous combination of anode and cathode materials are those that will be lightest and give high cell voltage and capacity. The general requirements for the anode, cathode and the electrolyte are given in Table 1.1.

Table 1.1 Anode, cathode and electrolyte requirements for a good cell

Anode	Cathode	Electrolyte
Efficiency as a reducing agent High coulombic output (Ah/g) Good electronic conductivity Stability (when contact with electrolyte) Ease of fabrication	Efficient oxidizing agent High coulombic output (Ah/g) Good electronic conductivity Stability (when contact with electrolyte) Ease of fabrication	Good ionic conductivity Zero electronic conductivity Does not react with electrodes Little change in properties with temperature Safeness in handling

1.2 Theoretical Cell Voltage and Capacity

The theoretical voltage and capacity of a cell are a function of the anode and cathode materials.

1.2.1 Free Energy

Whenever a reaction occurs, there is a decrease in the free energy of the system, which is expressed as

$$\Delta G_0 = -nFE_0 \quad \text{----------} \quad 1.1$$

where

n = Valency of the conducting species

F= Faraday constant (=96500 C or 26.8 Ah)

E_0 = Standard potential, (in Volts)

1.2.2 Theoretical Voltage

The standard potential of the cell is determined by its active materials and can be calculated from free-energy data or obtained experimentally. The standard potential of a cell can be calculated from the standard electrode potentials as follows (the oxidation potential is the negative value of the reduction potential).

Anode (oxidation potential) +Cathode (reduction potential) = Standard cell potential.

As an example, in the reaction of

$$Zn + Cl_2 \longrightarrow ZnCl_2$$

$$\begin{array}{lll} Zn \longrightarrow Zn^{2+} + 2e & & -(-0.76)\ V \\ Cl_2 \longrightarrow 2\ Cl^- - 2e & & \underline{(1.36)\ V} \\ & & 2.12\ V \end{array}$$

The theoretical standard cell potential for Zn/Cl_2 system will be 2.12 V.

1.2.3 Theoretical Capacity

The capacity of a cell is expressed as a total quantity of electricity involved in the electrochemical reaction and defined in terms of coulombs or ampere-hours. The "ampere-hour-capacity" of a battery is directly associated with the quantity of an electricity obtained from the active materials. Theoretically, one-gram equivalent weight of material will deliver 96500 C or 26.8 Ah (A gram-equivalent weight is the atomic or molecular weight of the active material in grams divided by the number of electrons involved in the reaction).

The theoretical capacity of a battery system, based only on the active materials participating in the electrochemical reaction, is calculated from the equivalent mass of reactants. As an example, the specific capacity of the lithium anode can be calculated as follows:

Lithium atomic weight is = 6.94 g

Number of electrons involved in the electrochemical reaction is = 1

Equivalent weight = Atomic weight/Number of electrons involved in the reaction

Equivalent weight of lithium = 6.94 g/1 = 6.94 g

Theoretical specific capacity = 26.8 Ah/6.94 g = 3.86 Ah/g

The capacity of the battery is also considered on energy (Watt-hour) basis by taking the voltage as well as the quantity of electricity into consideration.

Watt-hour = Voltage (V) x Ampere-hour (Ah).

1.2.4 Voltage Definitions

When a cell or battery is discharged, its voltage is lower than the theoretical voltage. The difference is caused by IR (internal resistance) losses due to a cell (or battery) resistance and polarization of the active materials during discharge [3]. This is illustrated in Fig. 1.2. In the idealized case, the discharge curve of a battery proceeds at the theoretical voltage until the active materials are consumed and the capacity is fully utilized. The voltage then drops to zero. Under actual conditions, the discharge curve is similar to the other curves in Fig. 1.2.

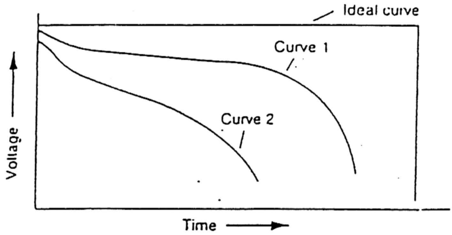


Fig. 1.2. Characteristic discharge curves [ref: 3]

The initial voltage of the cell under a discharge load is lower than the theoretical value due to the internal cell resistance and the resultant internal resistance (IR) drop. This initial drop in voltage during discharge is due to the increase in cell resistance. This is attributed to the accumulation of discharge products and polarization. Curve 2 is similar to curve 1, but represents a cell with higher internal resistance or a higher discharge rate, or both, compared to a cell represented by curve one. As the cell resistance or the discharge current is increased, the discharge voltage decreases and the discharge shows a more sloping profile. The temporal drop in voltage can also be attributed to the electrodes made from intercalation compounds. When the stoichiometry of the compound changes due to structural changes during discharge, the voltage across the cell also changes. Thus apart from IR drop, the voltage of the cell can also drop due to such phase changes encountered by the electrode materials.

1.2.4.1 Some Definitions About Different Voltages [3]

1. The theoretical voltage is a function of anode and cathode materials, composition of the electrolyte, and temperature.
2. The open-circuit voltage is the cell voltage under a no-load condition and is usually in close approximation to the theoretical voltage.
3. The closed circuit voltage is the cell voltage under a load condition.
4. The nominal voltage is one that is generally accepted as typical of the operating voltage of the cell, as, for example, 1.5 V for zinc-carbon cell.
5. The working voltage is more representative of the actual operating voltage of the cell under load and will be lower than the open-circuit voltage.
6. The average voltage is the voltage averaged during the discharge
7. The mid-point voltage is the voltage at approximately half the discharge time of the cell.
8. The end voltage is designated as the end of the discharge. Usually it is the voltage above which most of the capacity of the cell has been delivered. The end voltage may also be dependent on the application requirements. This is also called the cut-off voltage

1.3 Why Lithium Batteries?

The most important parameters for better battery performance are as follows [4]

1. High open circuit voltage
2. Low decline of cell voltage during discharge

3. Low cell resistance and polarization loses at the electrodes
4. High specific energy (Wh/kg) and specific power (W/kg)
5. Wide operating temperature range
6. Long operating life
7. Ability to withstand over charge and over discharge
8. Low self-discharge rate
9. Long shelf life
10. Guaranteed safety in use
11. Low cost

Most of the commercially available batteries may not satisfy the above demands. The batteries based on Ni-Cd, Ni-Metal Hydride, Lead-acid, Zinc-Carbon etc all have low specific capacity. The open circuit potential of these batteries is limited to 1.23 V (theoretically). This is due to the use of aqueous based electrolytes. The self-discharge rate in these batteries is high and they have a short shelf life. They also create memory problems. The use of batteries containing cadmium and mercury has pollution effects both at the production and disposal stages.

The substitutes for the above said batteries have to be developed. Such substitutes can be developed with lithium based systems. Lithium is the lightest metal in the periodic table and has the highest specific capacity. The specific capacity of a lithium metal is 3.86 Ah/g. The small ionic radius of the lithium ions can provide high volumetric capacity. The electrochemical potential for a lithium system is higher than the other systems i.e. 3.01 V for Li/Li^+.

Thus the interest is redirected from usual systems to lithium based system. Intensive research since the early 60s and 70s [5-9] succeeded with primary lithium batteries. Fig. 1.3 presents the theoretical specific energy with equivalent weight for the systems shown. Fig.1.3 clearly illustrates the advantage of lithium batteries over other battery systems present in the market.

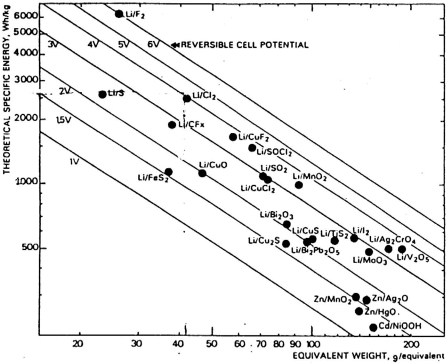


Fig. 1.3: Relationship between the equivalent weight (anode plus cathode) and the theoretical specific energy on weight basis of various electrochemical systems [ref: 10].

From Fig. 1.3, we can calculate the equivalent weight and identify the capacity in Wh/kg. The equivalent weight of lithium is 6.94 g and the equivalent weight of chlorine is 35.5 g. The equivalent weight of a couple is 42.44 g. This has been in well agreement with the value reported in the graph. The theoretical specific capacity in Ah/kg will be 26.8 Ah/0.04244 kg = 631.5 Ah/kg. Since the Li/Cl$_2$ couple gives 4 V, the theoretical specific energy in Wh/kg is 631.5 Ah x 4 V = 2526

Wh/kg is agreement with the results reported in the graph. As a second example, consider the Li/F_2 couple. The equivalent weight of the couple is ~26 g. Hence the theoretical specific capacity is 1033 Ah/kg and hence the theoretical specific energy is 6198 Wh/kg.

1.4 Why Polymer Electrolytes?

Many of the commercial batteries are employing electrolytes, which are based on liquid. To have a better battery, the principal requirements are long life, high efficiency, reliability, charge retention and freedom from maintenance [11]. None of the existing batteries (Ni-Cd, Ni-Metal Hydride, lead-acid etc) based on liquid electrolytes fulfils all these requirements at low overall cost and there is a need for research and development on new battery systems specifically designed for high energy density with alternative electrolytes and electrodes.

Many of the problems associated with primary batteries have been ascribed to the presence of the liquid-electrolyte phase. These problems include cell leakage, corrosion, self-discharge process, drying out of the cell, loss of electrolyte at elevated temperatures and severe restrictions on the capability for useful discharge at very low temperature [12]. Thus interest in solid state batteries are motivated in part by the hope that these problems would be minimized when the liquid electrolyte is replaced by a solid electrolyte. These solid electrolytes include not only the inorganic crystalline compounds [13-17] but also the ion conducting glasses [18-27] and ceramics [28-30]. With the introduction of intercalation mechanism in Li-ion batteries, the volume expansion during charging is an unavoidable phenomenon.

This volume expansion in batteries which uses the above said solid electrolytes will led to a shear stress with loss of contact or crack propagation even when the exchange of electrical charge is small. On the other hand, the use of liquid electrolytes has many disadvantages such as reduced electrochemical stability window, excess volume change (exfoliation), volatile and hazardous. Thus, there is a need for a solid electrolyte, which is flexible and plastic in nature to improve the above said problems. Such a solid electrolyte can be obtained by using polymers as a host for solid electrolytes. The first attempt in this aspect was given by Wright et al [31] but their potentiality was demonstrated by Armand et al. [32].

1.5 Types of Ion Conducting Polymers

Ionically conducting polymers [33] can be described as polar macromolecules in which one or more of a wide range of salts have been dissolved. Generally, polymers are insulators with long range order. The insulating polymers were made to conduct deliberately by introducing large concentration of ions into the polymer structure and that structure is designed to give the incorporated ions a high mobility [33-34].

The ion-conducting polymers were classified according to the way in which ions can be incorporated. Table 1.2 provides the information regarding the types of polymer electrolytes

Table 1.2 Types of ion conducting polymers

Type	Composition	Mobile species	Examples	Conductivity s/cm	References
Gel polymer electrolytes	Polymer, salt and solvent	Cations, anions and solvent	PAN + PC + $LiClO_4$	$\sim 10^{-4}$	35,36
Ionomer or polyelectrolytes	Polymer salt	None unless wet	Nafion	~1	37
Solvating polymer	Polymer solvent +salt	Cations and Anions	PEO + $LiClO_4$	$\sim 10^{-8}$	38,39
Solvating ionomer	Polymer solvent/salt	Cations or anions	------------------	------	40

PAN: Poly (acrylonitrile) PC: Propylene carbonate

PEO: Poly (ethylene oxide)

Gel polymer electrolyte is simply a polymer swollen with a solution of a salt in a liquid solvent. The salt dissolved in the liquid, which in turn is in solution in the polymer. Next, the polymeric salt concept, in which anionic (e.g. $-CF_3SO_3^-$) or cationic (e.g. $-R_3N^+$) groups bound to the polymer chain act as counter-ions to small, unbound and potentially mobile ions. The third type is the solvating polymer. Here, the polymer itself has the ability to dissolve certain salts and support the ionic mobility. Solvating ionomers is simply a soluble polymer used as surfactants.

1.6 Essential Requirements of Good Polymer Electrolytes

1. The polymer electrolytes must have an electrochemical stability domain extending from 0 V to as high as 4.5 V
2. Chemically compatible with the Li anode and cathode materials.
3. Good thermal stability
4. Good dimensional stability (in order to make it as a thin film)
5. Withstand electrode stack pressure in a cell as well as stress caused by morphological changes, which the electrolytes undergo during cycling of secondary Li-batteries. [41].

However, to expect both, the ionic conductivity of a liquid electrolyte and the dimensional stability of a solid in the same polymer electrolyte are to expect the coexistence of two properties, which are largely mutually exclusive. Nevertheless, a remarkable progress has been achieved in developing electrolytes with both of these properties via fundamental breakthrough and clever manipulations of electrolyte structures.

1.7 Mechanisms of Ion Conduction

Since the discovery of ion conducting polymers, the mechanism of ion conduction in polymers has been an issue. When Armand [32,42] presented his results, he was influenced by the knowledge of the conduction process in conventional crystalline solid electrolytes and therefore envisaged that transport within the ionically conducting polymers occurs in the crystalline regions. Later through NMR studies, Berthier et al [43] showed that ionic transport occurred within the amorphous regions.

Generally, polymers are classified as materials based on covalently bonded chain structures formed by the repetition of similar units. The chains are of sufficient length to confer on the material some additional properties not possessed by the individual units. In the molten state or in solution, these polymer chains are randomly coiled and even when apparently solid the randomness persists within a polymer. Crystallization is initiated at many locations and crystalline domains that develop are not coherently oriented with respect to each other. This means that there are portions of each long chain molecules that cannot be aligned within an individual crystalline region and these portions remain amorphous. This is shown in Fig. 1.4. Consequently polymers exhibit mixed morphology. Because of this mixed morphology, the conduction mechanism is complicated.

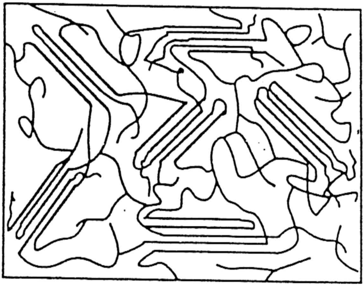


Fig. 1. 4. Mixed morphology in polymeric materials [44,45]

Usually, the kinetics and mechanism of electrochemical process in polymer electrolyte is studied by ac-impedance spectroscopy [46-49]. The conduction mechanism of the polymer electrolyte was predicted by analyzing their temperature behaviour. A fundamental assumption in theories of cationic transport in high molar mass polymer electrolyte is that, the net displacement of the "center of gravity" [50] of the polymer chains is not significant, long range cation transport must involve dissociate steps in which cations are transferred between neighboring coordinated sites located either on the host molecules or on the adjacent host molecule; i.e. the polymer segmental motion arising from bond rotation provides only for a short range motion of coordinated cations within limited regions of space [50]. This large-amplitude segmental motion of a polymer backbone will takes place only in the amorphous regions of the polymer electrolyte. Since the polymer segmental motion is largely frozen in crystalline phases, conductivity of crystalline polymer electrolyte is usually very low. The motion of the cation is coupled to the motion of the polymer segments [51].

Usually, anions do not form strong bonds with any of the polymer host commonly studied, so that their transport (where the ion association is not dominant) is likely to depend principally on the short-range polymer dynamics. Fig. 1.5 shows the relationship between the conductivity, glass transition temperature and with degree of crystallinity. The Fig. 1.5 shows that the ionic conductivity of the polymer electrolyte is increasing with decreasing crystallinity but the glass transition temperature is increasing. This shows very clearly that the ionic conductivity is inversely related to the crystallinity of the compound. The increase in T_g is only for the unplasticized polymer electrolyte system.

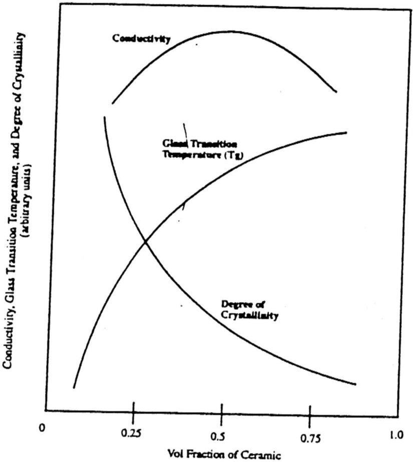


Fig.1.5. Ionic conductivity and its relationship with T_g and crystallinity

Fig. 1.6 represents the measured conductivity at ambient temperature, contributions from ion hopping, polymer chain motion, and transport number. Fig. 1.6 shows that the ion conduction in polymer electrolyte is due to three phenomena. In order to explain the ion conduction mechanism as shown in the Fig. 1.6, several theories have been proposed.

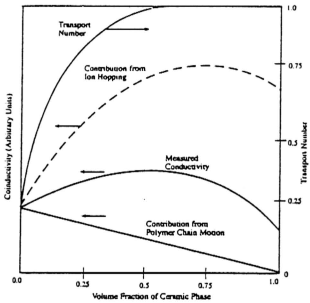


Fig.1.6. Ionic conductivity and its relationship with ion hopping and polymer chain motion

1.7.1 Solid State Theory (Arrhenius Equation)

Below the glass transition temperature, the variation of log σT with 1000/T shows linear behaviour, which can be expressed according to the Arrhenius, equation

$$\sigma T = \sigma_0 \exp\,[-E_a/kT] \qquad \text{----------} \qquad 1.2$$

Here, σ_0 is the pre-exponential factor,

E_a is the activation energy,

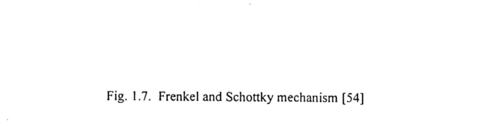
k is the Boltzman constant and

T is the absolute temperature

This clearly indicates that the conductivity mechanism in these polymeric materials is similar to that of ionic crystals. In ionic crystals, two types of defects namely Schottky and Frenkel defects, are responsible for ion transport.

1.7.1.1 Schottky and Frenkel Mechanism

In Schottky defects, positive and negative ions leave their normal sites due to their thermal agitation and create vacancies, Fig. 1.7. In Frenkel defects, an ion moves to the interstitial positions leaving a vacancy at its lattice. Some polymer electrolytes follow Arrhenius behaviour throughout the temperature range but with two activation energies [52-53] indicating a change in the nature of the material but not in the conductivity mechanism.



(a) Frenkel-type defect (b) Anti-Frenkel-type defect (c) Schottky-type defect

Fig. 1.7. Frenkel and Schottky mechanism [54]

1.7.2 Free Volume Theory (Vogel-Tamman-Fulcher Equation)

In some cases, the plot of log σT versus 1000/T follows a linear Arrhenius relationship at low temperatures but takes the shape of a curve at high temperatures. Thus at low temperatures, the conductivity mechanism is similar to that of ionic crystals. A different mechanism has been proposed for the behaviour at high temperatures [55-57]. This mechanism has been refered to as the free volume theory and can be described by the Vogel- Tamman- Fulcher (VTF) equation. The free volume approach involves co-operative mechanism of the molecular chains. The free volume fraction 'f' is given by the ratio of the volume of vacancies to the total volume. It has been shown that the free volume fraction is a linear function of temperature in most elastomers, at least in the range of $T_g < T < (T+100)$ [58].

The free volume fraction, 'f' is given by

$$f = f(T_g) + \alpha(T - T_g) \qquad \text{----------} \qquad 1.3$$

or

$$f = \alpha(T - T_0) \qquad \text{----------} \qquad 1.4$$

T_0 is the ideal transition temperature a purely mathematical parameter indicating the temperature at which 'f' extrapolates to zero. α is the thermal expansion co-efficient of the free volume fraction. $f(T_g)$ is the free volume fraction at T_g and below this temperature, where inter-chain bonding ensures an immobile structure.

A displacement of a chain segment or other diffusing unit depends on the availability of a sufficient large vacant space, v*(the activation volume) in the immediate vicinity. The actual vacant space adjacent to the unit varies around a mean value [59] which is given by the product of the free volume fraction, 'f', the effective volume, v, of the chain segment, and a geometrical correction for overlap, g, which is on the order of unity. The mean free volume per segment is much smaller than v*, but occasionally a free volume of v* or greater appears according to a probability, P

$$P = \exp.\ (-v^*/gvf) \tag{1.5}$$

$$P = \exp.\ (-v^*/gv\alpha(T-T_0)) \tag{1.6}$$

$$P = \exp.\ (-B/(T-T_0)) \tag{1.7}$$

where $B = v^*/g\alpha v$

This probability is a common factor in all forms of transport, mechanical, diffusive and electrical properties. Thus the fluidity, $1/\eta$, diffusion coefficient, D, and conductivity, σ, may all be written in the Vogel, Tamman and Fulcher (VTF) form [60] as

$$W(T) = W_0 \exp(-B/(T-T_0)) \tag{1.8}$$

Where

$W(T) = DT^{-1/2}$ or $\sigma T^{1/2}$ or $1/\eta$ etc and

W_0 is the appropriate pre-exponential factor: For example, the equation for conductivity is

$$\sigma T^{-1/2} = A \exp.\ \{-E_a/R\,(T-T_0)\} \tag{1.9}$$

This equation is analogous to the Arrhenius formula used for diffusion and conductivity in crystalline solids. The most important term is T_0; this should be as low as possible for fast ion conduction.

1.7.3 WLF Equation

To eliminate the unknown T_0 and the pre-exponential factor, polymer scientists normally use the Williams, Landel and Ferry (WLF) equation to compare properties at a reference temperature, Tr. This is derived from the free volume theory.

$$\ln \frac{W(T)}{W(T_r)} = -B \quad \frac{1}{T-T_0} - \frac{1}{T_r-T_0} \qquad \text{----------} \qquad 1.10$$

T_0 is eliminated by a parameter transformation.

$C_1 = B/(T_r-T_0)$; $C_2 = T_r-T_0$

$$\ln \frac{W(T)}{W(T_r)} = \frac{C_1\,(T-T_r)}{C_2 + (T-T_r)} \qquad \text{----------} \qquad 1.11$$

The reference temperature, T_r may be chosen anywhere between T_g and T_g +50^0C, according to experimental convenience. Thus a property can be specified over a wide temperature by tuning C_1 and C_2 to give the best data fit. In summary the conductivity mechanism can be represented pictorially (Fig. 1.8) as suggested by Souquet et al [57]. The polymer segmental motion may also be pictorially (Fig. 1.9) represented by Souquet et al [57].

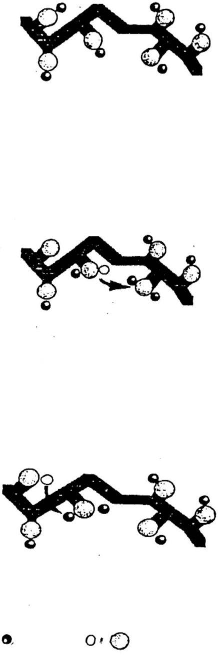


Fig. 1.8. Charge carriers activated migration [ref: 57]

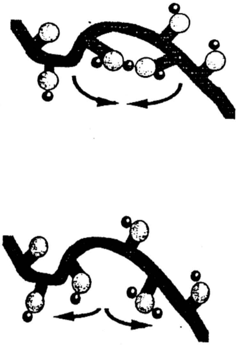


Fig. 1.9. Cooperative migration with chain movements [ref :57]

1.7.4 Bruce's Theory on Ion Conduction Mechanism

A long established view in the field of polymer electrolytes has been those cations larger than Na$^+$ can only exist outside the PEO helix. The study by Bruce [61] has shown some contrasting evidence, which suggests that cations ranging in size from Li$^+$ (0.76 Å) to Rb$^+$ (1.52 Å) might be accommodated within the helix. This hints at the possibility of cation transport along these tunnels in fashion reminiscent of the original view of Armand [32,42], but with essential addition that the dynamics of the chain in the amorphous state above T$_g$ facilitates ion transport along the chain. This could involve a mode, which expands and contracts the chain along their axes. It was also found that there is no evidence of ion cross-linking between neighboring chains. The chains are essentially isolated from each other. When salt is added to the polyether, the ions form intra rather than interchain cross-links, and that such intrachain cross-linking is largely responsible for stiffening the chains and hence the increase in T_g with increasing salt concentration.

1.7.5 The Microscopic Approach of Ion Transport in Glasses

Anderson and Stuart [62] developed a model for ionic conduction in silicate glasses. Basically, an ion is supposed to leave a non-bridging oxygen for another vacated or empty site. In a first approximation, the activation energy of the ionic conductivity process will be assumed to be the energy required to move the ion, presupposing that the structure remains unchanged, plus the energy required to deform the structure by generating a hole large enough for the ion to pass. According to this model, the activation energy, E_a consists of sum of two different energy terms

$$E_a = E_b + E_s$$

where E_b is the electrostatic binding energy and E_s is the strain energy.

1.7.6 Ion Conduction Mechanism in Plasticized Polymer Electrolytes

In the case of plasticized polymer electrolytes, the conduction mechanism is even more complicated. The key to the development of solid polymer electrolytes with ionic conductivities approaching that of their liquid electrolyte counterpart is to modify the electrolytes in such a way to increase both mobility and concentration of the ionic charge carriers. This can be achieved by adding low molecular weight organic solvents preferably of high dielectric constant.

The organic solvents are called as plasticizers. In polymer language, the term plasticizer refers to a species, which will decrease the glass transition temperature of a polymer [63-64]. It was shown at an early stage in the development of polymer electrolytes that lower glass transition temperatures resulted in higher conductivities, since it was believed, that the mechanism of ion conduction was strongly coupled to the segmental motion of the polymer backbone [65]. It has been shown that at salt concentration levels used, ionic aggregation also plays a major role in limiting the conductivity by decreasing the available number of charge carriers [66-67]. This is a result of low permittivity polyethers. Therefore, the addition of plasticizers with higher relative permittivities may have an additional effect on the ionic conductivity of polymer electrolyte. The role of the plasticizer in the polymer electrolyte is, to reduce the crystallinity of the parent polymer, lower the electrolyte viscosity and increase the ionic mobility by reducing the potential barrier to ionic motion and to dissociate the Li salts thereby increasing the number of charge carriers.

In traditional sense, plasticized polymer electrolytes are not true polymer electrolytes. The plasticizer solvents may themselves complex Li^+ and cause the motions of the ions to be substantially decoupled from that of polymer chain motion. These polymer electrolytes are also called "gel electrolytes". When the plasticizer is mixed with the polymer electrolyte, the ionic conductivity of the polymer electrolyte is increased to certain extent. The ionic conductivity 'σ' of an electrolyte is

Table 1.3 Some plasticizers and their properties

Plasticizer	Dielectric constant	Viscosity (cp)	Boiling point (^{0}c)
Propylene Carbonate	64.4	2.53	241
Ethylene Carbonate	89.6 (40^0 C)	1.85 (40^0 C)	248
γ-butyrolactone (BL)	39.1	1.75	202
N-methyl pyrrolidinone	32	1.66	204

1.8 Solid State Batteries

As early as the turn of the century it was recognized that there exists solid electrolytes, that is solid compounds with practically pure ionic conductivity. This was first established by transference number measurements [68-75]. Thermodynamic studies [76-79] also suggest that some solids can function as electrolytes. In the recent past considerable progress has been made in the development of practical solid state batteries as energy sources. Various authors [80-91] have reviewed the historical developments and some recent advances in this field. Table 1.4 provides the advantages and disadvantages of the solid state batteries.

Table 1.4. Advantages and disadvantages of solid state batteries

Advantages	Disadvantages
Excellent storage stability and shelf life of 10 years or better	Low current drains
High energy densities	Power output reduced to low temperature
Hermetically sealed-no gassing or leakage	Components degrade in normal ambient conditions
Wide operating temperature range up to 200^{0}C	
Shock and vibration resistant	

1.8.1 Disadvantages

Because of a sudden surge in interest in solid state batteries, the development of solid electrolytes is a very important aspect. A large number of solid electrolytes have been developed. Since the ionic conductivity of these materials is associated with the amorphous phase, ionic conducting glasses were prepared and analyzed. The disadvantages with solid electrolytes are as follows.

1.8.1.1 Volume Change

Dimensional changes always occur during discharge of a battery since the electrode chemicals are reacting to form a discharge product. In the absence of a liquid electrolyte phase, deformation of the cell can result with swelling or shrinkage of electrodes, cracking of the electrolyte and possible shorting of the cell [12].

1.8.1.2 Electrolyte Impedance

The high impedance of solid electrolytes remains a problem because it restricts the solid state batteries to very low current densities at ambient temperatures [12].

1.8.1.3 Discharge Product Impedance

The discharge product as it forms between the electrode has high impedance. Even if one fabricates a solid state battery with high conductive solid electrolyte separating the electrodes, the reaction product, which may form as a layer between the electrodes and the electrolyte or be incorporated into the cathode structure, can still contribute to the overall internal cell resistance of the battery [12].

1.8.1.4 Materials Compatibility

Compatibility of the electrodes with the electrolyte must be adequate with all types of battery design. In solid state batteries, this requires that the cell potential be less than the decomposition potential of the electrolyte, or else solid state reactions will occur at the interface, generating a variety of decomposition products [12].

1.8.1.5 Manufacturability

Manufacturing problems with solid state batteries are those associated with the use of powdered, highly reactive materials that can be decomposed by the ambient conditions. Sensitivity towards moisture, oxygen or nitrogen requires that manufacturing be done in controlled atmosphere enclosures. The final battery must be hermetically sealed to prevent degradation during extended operating or storage times.

1.9 Lithium Primary Batteries with Non-aqueous Electrolytes

Due to the disadvantages of the solid state batteries, the lithium based primary batteries were constructed with non-aqueous electrolytes. The research is once again directed towards liquid electrolytes but with non-aqueous based organic solvents. Lithium organic liquid electrolyte batteries have gained considerable importance because of their high energy densities and have found potential applications in a variety of terrestrial and space applications [10]. Due to their high capacity, lithium primary batteries based on non-aqueous organic electrolytes are available in the market, which includes Li/SO_2, Li/V_2O_5, Li/(CF)x, Li/MnO_2, Li/FeS_2, Li/CuS and Li/CuO. All of these chemical couples except the Li/SO_2 system deal with cathodes making it possible for them to form the basis of solid state batteries. The use of organic electrolytes in primary lithium batteries is due to the following reasons.

(a) higher rate capabilities,

(b) wider temperature range of operation (-41^{0}C to 70^{0}C),

(c) long shelf life, and

(d) low shelf-discharge

1.10 Lithium Metal Secondary Batteries

After the success of lithium non-aqueous primary batteries, research and development was directed towards lithium secondary batteries. The electrolytes used in the rechargeable lithium batteries are non-aqueous organic solvents in which the lithium ion conducting salts such as $LiClO_4$, $LiBF_4$, $LiPF_6$ etc were dissolved. In the early 70s, it was discovered that intercalation compounds could be used as electrodes in secondary Li-batteries.

During 1970s and 80s almost all work on secondary lithium battery electrodes centered on the use of intercalation compounds as the positive electrodes (cathodes) and metallic lithium or lithium alloys for the anodes. Of these, the rechargeable Li/MnO_2 "Molicell" in the 80s was probably the most sophisticated product. Apart from a few small-size secondary coin cell products, these AA size larger cells have proven very difficult to make safe and there has been incidents of fires in equipment powered by secondary Li/MoS_2 cells which led to a product recall [92,93].

1.11 Disadvantages of Secondary Lithium Batteries

The poor safety of secondary Li-cells with metallic Li-anodes can be understood. The surface area of the negative electrode, and hence the area of contact between the lithium and the electrolyte gets larger and larger as the cells are cycled. Since this interface is not thermodynamically stable, the cells become increasingly sensitive to thermal mechanical and electrical abuse [94]. Dendrite growth on the surface of the lithium metals short circuit the battery [10]. Thus, the secondary battery with lithium metal anode was not very successful.

1.12 Lithium Ion Batteries or Rocking-Chair Batteries

The poor safety of the lithium metals in secondary lithium batteries directed research towards a new way of developing lithium batteries without lithium metal. The concept is based on the lithium ion rocking-chair mechanism in which the Li-ion rocks between the anode and cathode. In lithium ion rocking chair cells, intercalation compounds were used as electrode materials. In all of the insertion reactions of alkali metals, the charge transfer takes place from the alkali metal to the host structure. This charge transfer can be small (e.g. graphite) or nearly complete (e.g. TiS_2). The EMF of the Li/host couple is determined primarily by the degree of charge transfer with higher potentials for higher charge transfer. The rechargeability of the cells is closely tied to the reversibility of the insertion reaction. The reversibility tends to be best when structural differences between the host and the insertion compounds are minimized.

1.13 What is Meant by Intercalation?

Graphite is the oldest and one of the most versatile intercalation host. Graphite is capable of intercalating both strong electron donors and acceptors. The first reported intercalation compound was graphite sulfate by Schauffautl in 1841[95]. Its use in secondary batteries was discovered only in 1970s. An Intercalation 'host' is a solid, which can reversibly incorporate 'guest' atoms or molecules within its crystal lattice with only small structural changes. Fig. 1.10 schematically shows the intercalation mechanism that takes place in Li-ion cells.

The electrode reaction which occur in a Li/Li_x (HOST) cell, where Host is an intercalation cathode, are:

$$LiMO_2 + C_6 \longleftrightarrow \square\, MO_2 + LiC_6$$

There are still uncommon electrochemical systems, which may be described as concentration cells where Li-ions rock from one electrode side to the other. Accordingly, these cells have been termed "rocking chair cells" [96]. Because of the sudden surge of interest in intercalation compounds, a variety of insertion compounds have been synthesized, characterized and analyzed [97-105].

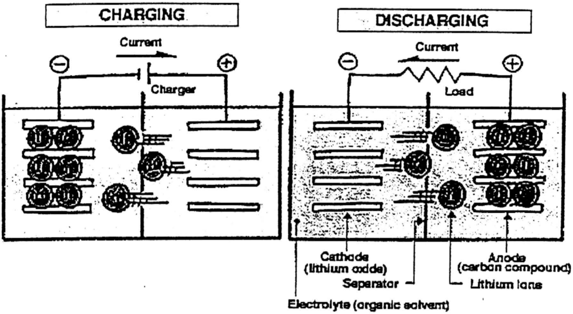


Fig. 1.10. Lithium intercalation mechanism

1.13.1 Criteria for Selecting Insertion Electrodes [106].

1. The lithium activity in the negative electrode $Li_xB_nC_m$ must be close to '1' in order to assuring open circuit voltages approaching those obtainable with pure lithium.
2. The equivalent weight of both the electrodes must be low in order to assure specific capacity values of practical interest
3. The diffusion coefficient of Li^+ ions in both the lithium source $Li_{1-x}A_zB_y$ positive electrode and in the lithium sink $Li_xB_nC_m$ negative electrode must be high to assure fast kinetics of the electrochemical process and thus fast charge and discharge rates

4. The voltage changes upon lithium ion uptake and release must be small in both electrodes to limit fluctuations during charge and discharge cycles.
5. Both the ion source and the ion sink electrode must be easy to fabricate and based on nontoxic compounds, to assure low cost and environmental control.

To meet these conditions satisfactorily, insertion compounds must be selected with properties consistently different from those normally used for the conventional lithium batteries. For instance, conditions '1' and '2' can be achieved only by using innovative materials that could assure Li-insertion voltages approaching zero (versus Li). The most popular in this respect are graphite-type insertion compounds. Further more, the achievement of the previously mentioned crucial conditions require the selection of both low-voltage negative and high voltage positive electrodes. The most convenient compounds are having lithium insertion voltage at around 4V-namely, layered lithium metal oxides of $LiMO_2$ type, where M= Co or Ni, and three-dimensional, spinel-type lithium manganese oxides. By switching over from Li to graphite leads to some tradeoffs, but the advantage of the graphite anode over metallic lithium, especially in cost, cycle-life and safety far out weigh its disadvantages (if any) [94].

1.14 Advantages of Graphite Anodes

The specific capacity of Li is 3.86 Ah/g and its density is 0.51g/cc. The maximum amount of lithium can be intercalated into graphite is 1 Li per 6 carbons, yielding specific capacity of 0.372 Ah/g. The density of graphite is 2.2 g/cc, but practical powder electrodes normally are the order of 50% bulk density, so an electrode density for carbon of about 1 g/cc is reasonable. At first glance, it appears that the substitution of carbon for Li will lead to a large penalty in energy density. However, it is not the case.

The advantage of metallic lithium anode is between 50 and 100 cycles in the best case. This means about 1% of the lithium anode is consumed on each cycle of the cell. Therefore, to attain a cycle life of 500 cycles, cells with metallic lithium anodes require 5 to 6 fold stoichiometric excess of Li compared to that needed to fully intercalate the cathode. By contrast, the cycling efficiency of the carbon electrode is nearly 100%, and no excess anode is included in Li-ion cells, even for those which attain 1200 cycles [107]. Practically the specific capacity of metallic lithium is obtained from the theoretical one by dividing by a factor of five or six, which gives about 0.75 Ah/g and 0.37 Ah/cc for metallic lithium. The corresponding numbers for graphite in a practical anode configuration are about 0.230 Ah/g (taking the current collector and binder in to account) and about 0.330 Ah/cc. For small cells, where the volume is constrained, the replacement of carbon anode incurs almost no capacity penalty, with the small weight penalty. Experience with prototype cells confirms with these arguments [108-109]. The replacement of graphite did not have much effect on the capacity of the cell.

1.15 Intercalation in Graphite

Much of the early work is focused on the intercalation of alkali metals with graphite. Fig. 1.11 (a) schematically shows the structure of 'n' graphite layers and one intercalant layer. The Fig. 1.11 (b) shows the in-plane structure of stage 1 LiC_6.

From Fig. 1.11 (b) it is observed that the Li-atoms reside in the center of the Van der Waals gap centered in the carbon hexagons of the AAAAA stacked carbon sheets. The Fig. 1.11 (a) shows the structures of the stage-1, 2 and 3 compounds. Very little work has been carried out in disordered carbon materials. The reason for this has been summarized by Dresselhaus and Endo [110].

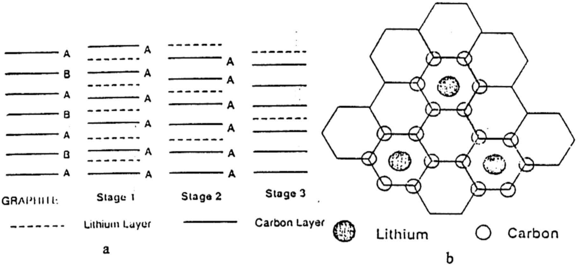


Fig. 1 11. (a) Structures of stage-1, 2 and 3 compounds and (b) in-plane structure of LiC_6 [94]

Intercalation is facilitated by a high degree of structural order of the graphite host material and retarded by defects, structural imperfections, and disorder. Good staging fidelity is achieved only in hosts with high degree of structural perfection. Thus the basic scientific studies on intercalated graphite fibers have focused on highly ordered graphite fiber host materials. Several authors have [111-112] reviewed the intercalation of alkali metals with graphite. This limiting stoichiometry with Li is LiC_6 and for K, Rb, and Cs is AC_8. In these limiting compositions the alkali metal is located between each graphite layer and is oriented as shown in Fig. 1.12. The interesting feature of graphite compound is staging. In the stage compound every second (stage 2) third (stage 3), etc layer is fully occupied with intervening layers vacant. For Li, only the stage '1' compound LiC_6 and stage '2' compound of variable composition LiC_{12} to LiC_{18} are known.

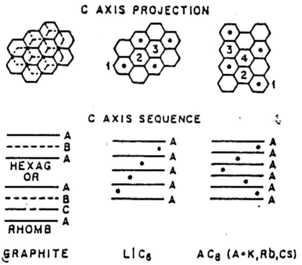


Fig. 1.12. Structures of graphite and first stage alkali graphite [ref: 113]

1.16. New Anode Materials for Lithium Secondary Batteries

Recently Nagayama et.al, [114] came up with a new electrode material for lithium secondary batteries. The material is $SnSO_4$. From the battery results, it can be observed that the specific capacity obtained from the study is close to 500 mAh/g. It is also observed that it is possible to intercalate four lithium atoms per formula unit of $SnSO_4$. This can be used as an anode material besides carbon. However, tin agglomeration limits its usefulness. Barium metaplumbate has also been used as anode for such batteries [115].

1.17 Objectives of the Present Work

The main aim of this work is to prepare a polymer electrolyte for use in solid-state polymer batteries. As such, poly (vinyledene fluoride), (PVDF) has been chosen as the polymer host material. PVDF is chosen as the polymer host for the present study due to a variety of advantages it has over other polymers. It is very easy to fabricate a freestanding PVDF polymer film with good mechanical strength. The ionic conductivity value obtained for a PVDF based polymer electrolyte is also high at ambient condition. Initial investigation on PVDF based polymer electrolyte [116-118] show only low ionic conductivity at ambient temperature. However, the latter studies on PVDF based polymer electrolytes [119-121] has shown a conductivity of 10^{-3}S/cm at ambient temperature. The thin-film batteries based on PVDF polymer electrolytes were constructed and analyzed [122-126]. The result from the previous studies shows good performance level for the batteries.

PVDF is a high molecular weight thermoplastic polymer with melting point between 120^0C and 160^0C [127]. It is also chemically inert. Hence it is highly resistant to oxidizing agents and halogens and is almost completely resistant to aliphatic, aromatics, alcohols, acids and chlorinated solvents. It is resistant to most acids and bases. It is a semi-crystalline polymer with piezo- and pyroelectric properties. A battery with a PVDF based electrolyte can therefore be used at elevated temperatures due to its high melting point. Other advantages of PVDF are its high mechanical and dielectric strength. It is thermal resistant to low temperatures, stable to ultraviolet and extreme weather conditions, self-extinguishing and non-toxic. PVDF combines typical fluoropolymer properties with the mechanical properties of more rigid thermoplastics. PVDF has a high purity, a high heat-deflection temperature, and UV and gamma radiation resistance. PVDF is used in semiconductor processing, chemical processing and heat exchangers. In this work, PVDF will be doped with lithium tetra fluoro borate, $LiBF_4$. $LiBF_4$ is chosen because of its low dissociation energy compared to $LiClO_4$. This low dissociation energy will give rise to a large number of free Li ions in the polymer electrolyte and thereby increasing the ionic conductivity. The anionic size of the salt is bigger than $LiClO_4$. This bigger anionic size will help to increase the ionic conductivity of the polymer electrolyte [67]. In polymer electrolytes, it has been reported that both cation and anion moves along the polymer backbone [51].

After selecting the polymer host and the salt used in the present study, the polymer electrolytes were prepared using the solution cast technique. When the films have formed, they will be characterized by X-ray diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS) and ac-impedance studies. In order to obtain high ionic conductivity at ambient condition, plasticizers will be added to the polymer electrolyte. The plasticizers used are Dimethyl Formamide (DMF), Methyl Formate (MF) and Ethylene Carbonate (EC). Since these plasticizers have a high dielectric constant and low viscosity, it will enhance the ionic conductivity at ambient condition. The polymer electrolyte will then be characterized for their thermal, structural and surface properties. Finally, batteries will be fabricated with the help of the above said plasticizer based polymer electrolytes and characterized.