CHAPTER I

GENERAL INTRODUCTION & LITERATURE SURVEY
1.1. GENERAL SCENARIO OF ENERGY REQUIREMENTS

Solid state ions are interesting phenomenon due to the wide range of interdisciplinary subject such as physics, chemistry and material science, which lead the way to accommodate curiosities of its application. In this regard, batteries, fuel cells, electrolytic cells, electro chromic devices, chemical sensors, thermoelectric converters or photo galvanic solar cells are solid state ionic devices of large practical interest. These devices are developed from a wide spectrum of solid state ionic material, ranging from inorganic crystalline and polycrystalline solids, ceramics, glasses, polymer, composites to nano-scale materials [1, 2].

Due to the elevating depletion of natural resources and increasing levels of environmental pollution of Earth’s atmosphere and oceans, energy-efficient technologies are in an ever-growing demand. In the wake of the energy challenges facing present and future generations, researchers are focusing on new ways to enhance the utilization of renewable energy sources and reduce the dependence on fossil fuels [3]. However, with the increasing reliance on green energy, comes the need for advanced energy storage technologies that are able to balance differences between the electricity demand of human beings and the fluctuating supply from alternative energy sources. Development of alternative, sustainable, clean energy technologies is needed to address this inevitable challenge. In this regard, solar, wind, hydrothermal, geothermal, nuclear, biomass, fuel cells, high energy density batteries and supercapacitors are becoming appealing.

Therefore, energy storage plays a vital role in our daily life, and has rapidly increasing importance in various applications. There are four types of energy storage technologies available based on mechanical, electrical, chemical and electrochemical
modes. Among these, electrochemical power source modes in general can be classified into three types such as batteries, fuel cells, and super-capacitors. Both the batteries and supercapacitors are energy storage devices, in which the active materials are an integral part of the device. On the other hand, fuel cell is an energy conversion device, in which the fuel and oxidant (active materials) are supplied to the electrochemical cell from an external source as and when required. Replacing the internal combustion engine (ICE) vehicles with electric vehicles (EVs) and hybrid electric vehicles (HEVs) is a possible way to mitigate CO$_2$ emission in the future. In this regard, Battery systems connected to large solid-state converters have been used to stabilize power distribution networks. The rechargeable batteries are at present a most promising energy storage device. Therefore, the development of rechargeable batteries with high energy density, high power density and high safety is of particular interest [4].

1.2. ENERGY STORAGE DEVICE- LITHIUM ION BATTERIES

Rechargeable Lithium-ion batteries represent the top of technology in electrical energy storage devices. Lithium-ion (Li-ion) batteries have been extensively studied in recent decades, due to their high energy and power density and low capacity fading. They were first introduced in 1970 by Whittingham, and then commercialized in 1991 by Sony Corporation [5]. Due to the high energy density of Li-ion batteries, they have been integrated into small portable devices such as laptops, cell phones, cameras, camcorders and MP3 players. Moreover, their application in electric vehicles is growing. Rechargeable lithium ion batteries involve a reversible insertion/extraction of lithium ions into/from a host electrode material during the charge/discharge process. The lithium insertion/extraction process, which occurs with a flow of ions through the electrolyte, is accompanied by an oxidation/reduction (redox) reaction of the host matrix assisted by a flow of electrons through an external circuit (Figure 1.1).
The open-circuit voltage $V_{oc}$ of such a lithium cell is given by the difference in the lithium chemical potential between the cathode ($\mu_C$) and the anode ($\mu_A$) as

$$V_{oc} = (\mu_A - \mu_C)/F,$$

where $F$ is the Faraday constant ($F = 96485 \text{ C mol}^{-1}$).

Figure 1.2 gives a schematic energy diagram of a lithium-ion cell at open circuit. The cell voltage is determined by the energies involved in both the electron transfer and the Li$^+$ ion transfer. While the energy involved in electron transferring is related to the redox potential of the ion involved in the cathode and anode, the energy involved in Li$^+$ ion transfer is determined by the crystal structure and the coordination geometry of the site into/from which the Li$^+$ ions are inserted/extracted [6]. The energy separation ($E_g$) between the lowest unoccupied molecular orbital (LUMO) and the highest occupied
molecular orbital (HOMO) of the electrolyte defines the stability window of the electrolyte. Therefore, thermodynamic stability considerations require the redox energies of the cathode ($\mu_C$) and anode ($\mu_A$) to lie within the band gap $E_g$ of the electrolyte, as shown in Figure 1.2. An anode with a $\mu_A$ above the LUMO will reduce the electrolyte, and a cathode with a $\mu_C$ below the HOMO will oxidize the electrolyte unless an appropriate solid electrolyte interfacial (SEI) layer is formed to prevent such reactions [6].

![Figure 1.2](image_url)

**Figure 1.2** Schematic energy diagram of a Lithium battery at open circuit voltage. HOMO and LUMO refer to the Highest Occupied Molecular Orbital and the Lowest Unoccupied Molecular Orbital in the electrolyte, respectively [7].

Thus, the electrochemical stability requirement imposes a limitation on the cell voltage as given by

$$V_{oc} = (\mu_A - \mu_C)/F \leq E_g$$
Advantages of lithium-ion secondary batteries

(a) High energy density
(b) High battery voltage
(c) Long charging-discharging cycle and
(d) No memory effect [8, 9].

1.3. SELECTION CRITERIA FOR LITHIUM-ION BATTERY SYSTEMS

For a commercial lithium ion battery system, the following requirements are essential [10]:

- The reactants must have sufficient energy content to provide a useful current and voltage level. The normal energy density for a lithium-ion battery is between 100 and 250 Wh kg\(^{-1}\) (energy per unit mass).

- For a general consumer battery, the battery operation temperature should be in the range of 0-40 °C and the storage temperature should be in the range of -20 to 85 °C.

- The materials must maintain their mechanical and chemical stability over time in the operating environment, avoiding, for example, reaction with the electrolyte or no irreversible phase change.

- A general lithium-ion battery must be capable of complete charge and discharge over 300 cycles with capacity loss less than 20 %.

- The cost of the battery should be affordable for the customer.

- All commercial batteries must be safe in the normal operating environment. Additionally, they should not vent hazardous materials, nor present any hazard under mild abuse conditions (e.g. leaking, explosion, etc).
1.4. LITHIUM-ION BATTERY TECHNOLOGY: CHALLENGES & NECESSITATE FOR RESEARCH AND DEVELOPMENT (R & D)

During the recent past, lithium primary cells have evolved to high energy rechargeable batteries present in our daily life and have accelerated the trend to an ‘all-electric-society’ with portable electronics and tool omnipresence. The need to diversify our sources of energy away from fossil fuels makes electricity, a noble form of energy, easy and efficient to convert to other forms and distribute, a perfect solution for modern societies including the important transportation sector and the electric vehicle. However, such a strategy calls for an efficient means of storage for this instantaneous form of energy [11].

The development of eco-greener, cheaper, and safer electrodes consists of lithium ion batteries, which is considered today as a goal and developments of strategic importance for energy storage technology. Lithium-ion batteries has been stands to be the undisputed winner among various rechargeable batteries (Ni-Cd, Ni-MH and Lead acid) in powering portable electronics and also recently for vehicle application. However, there are a few shortcomings and limitations namely.

- Li-metal plating occurs on the anode during the fast discharge. Hence, it is mandatory to have sophisticated electronic protection circuits which shall maintain current and voltage values within safe limits
- Subject to aging, even if it is not in use
- Expensive to manufacture owing to the material cost and Technology is not fully mature
- Stable electrolytes with low decomposition potential are required to withstand high potential (5 V)
CHAPTER-I

- Use of toxic and environmentally hazardous materials.

These aforementioned issues trigger serious research and development works to surmount the limitation and progress the technology to the next level. Considerable attempts have been carried out to find suitable electrodes with energy efficient, economic production process and environmentally benign materials [12].

1.5. ADVANCED TECHNOLOGIES: AS A NEXT ENERGY DEVICE

In the past 50 years, lithium has allowed the emergence of high energy, high power rechargeable batteries that have replaced most lead-acid and nickel-alkaline systems in portable applications. This commercial success has triggered a new interest for electric transportation from existing hybrid electric vehicles (HEVs) cars to plug-in HEVs and electric vehicles (EVs), now actively developed [13-15].

The increasing affinity of many advanced technologies is towards miniaturization that is the future development of batteries is aiming at smaller dimensions with higher power densities. The development of new technologies and miniaturization in the microelectronics industry has reduced the power and current requirements of small power electronic devices such as smart cards and other CMOS circuit applications [16]. Therefore, developing improved solid-state thin film batteries will allow better compatibility with microelectronic processing and components. In the modern past, research focus is directed towards the development of high performance lithium ion (Li-ion) hybrid electrochemical supercapacitors (Li-HEC) because of their higher power density than the rechargeable battery (e.g., Li-ion batteries) and higher energy density than supercapacitors (e.g., electric double-layer capacitors, EDLC). Thus, Li-HEC is expected to bridge the gap between the Li-ion batteries and EDLCs and become the ultimate power source for HEVs and EVs in the near future [17, 18].
1.6. SCIENTIFIC CHALLENGES ASSOCIATED WITH Li-ION BATTERIES

The major challenges associated with electrode materials of Li-ion battery are described by the following factors with their possible solutions. Due to their problems, the obtainable capacity is lower than the theoretical capacity and results in lower energy density that is insufficient for the intended applications. The low energy efficiency could arise due to large polarization, which becomes more severe at higher charge-discharge rates along with poor cyclic life due to capacity fading with successive cycles [19].

Low Conductivity and Thermal Runway

It is a well-known fact that most of the electrode materials bear low conductivities that cause poor conduction of electrons, which affect the storage of lithium. In addition, it is necessary that every material should have sufficient ability to efficiently receive the electrons and to deliver to the external circuit. Furthermore, due to low intrinsic conductivities, several materials have failed to utilize all of their redox sites, as no pathways exist for electron transfer between redox site and external circuit [20]. Incorporation of carbon or other highly conductive agent as outer coatings or part of inner structure will effectively overcome this problem [21]. Furthermore, the power of the battery depends strongly on internal impedance (impedance inversely interacts with power) and heat generated during operation. The heat generation inside the Li-ion battery is due to three main factors: interfacial kinetics (activation), species transport (concentration), and heat production by the movement of charged products/electrons (ohmic losses). The main heat generation happens due to the irreversibility in battery and from electrochemical reactions. The concentration gradient of species also affects the heat generation, but it is very small in well-designed batteries. By developing appropriate cell chemistries and control over voltage range, thermal issues can be resolved.
Morphological and Structural/Phase Changes

Lithium storage in several materials strongly depends on their morphology, thus if morphology of electrode material changes during lithium insertions and extraction, it could drastically affect the performance and cyclic life. Furthermore, any phase or morphological changes might cause the aggregation of newly segregated product resulting in loss of the electrical contact, ultimately leading to the destruction of cell operation. Further, the morphological changes also brings fresh surface of electrode materials in contact with electrolyte that rebuild the solid electrolyte interface film (SEI), which cause irreversible loss of capacity. Similar to morphological changes, several materials show crystal structure or phase changes during cycling process of electrode.

The newly formed crystal structure or phase thus behaves differently towards lithium storage. Most crystal structure changes cause poor electronic conductivity, sluggish kinetics towards lithium insertion and extraction; as a result of poor capacity and cyclic life. These structural changes are inherent to specific material at specified conditions. Nanoscience plays a critical role by developing nanostructures that strongly diminishes the structural changes by improving phase transformation kinetics [22].

Volume Changes and Thickness of Solid Electrolyte Interface Film

The volume changes of electrode materials during alloying and de-alloying with Li⁺ result in severe volume increase that produces strains in the electrodes. Thus, as a result, isolation of the electrode material from the current collector causes electrical insulation or short circuiting of cell. Further, due of electrical insulation, the inaccessibility of Li⁺ to access the redox sites in active materials cause drastic capacity fading and poor cyclic life. These volume changes are more associated with the high theoretical capacity materials such as Si, Ge, and Sn. Thus, reduction in size to nano,
outer protection coatings, void engineering, self-healing polymeric matrix and hard metal (Co, Ni, Fe, etc.) doping are the possible ways to resolve these problems. Furthermore, the organic electrolytes decompose at the working potential of $<0.5$ vs. Li/Li$^+$ and forms thin SEI film on the surface of electrode [23, 24].

This cause an irreversible loss of capacity, but, it is one fundamental part of battery operation that cannot be completely diminished. A good control over thickness of SEI film can be achieved by tuning the surface chemistry. However, the problems lie in the poor mechanical strength of SEI film, as it cannot bear any stress and thus cannot withstand any pressure or stress. The structural, morphological and volume changes in the electrode materials causes the breakdown of SEI film and exposure of the fresh electrode surface to the electrolyte, resulting in further decomposition of the electrolyte and fading of capacity [25].

Furthermore, the SEI film is an insulator (electronically) in nature and its regeneration increases the diffusion path for Li$^+$. To this day, there is no appreciable control over the chemical composition, grain size, thickness, and spatial distribution of the SEI film. In this case, nanostructures cause a big problem due to their high surface area and energies, by controlling these factors or protecting the surface with inactive metals or carbon coatings may result in better control over the SEI film [25].

1.7. A KEY ROLE OF THE ELECTRODE MATERIALS FOR LITHIUM-ION BATTERIES

The choice of electrode materials (anode or cathode) is an important factor in the performance of a cell, since; the electrochemical reaction in a cell is intimately tied to the electrode materials. The key parameters for electrode materials include voltage, gravimetric and volumetric energy density, power density, cycle life, safety, efficiency, cost, toxicity, etc.
The cycle life is defined as the number of charge/discharge (C/D) cycles the cell can perform before the specific capacity falls below a certain percentage of the initial capacity. The cycle life depends on many factors such as the structure stability of the electrode materials, the formation of the SEI layer and its stability, the stability of the electrolyte and the mechanical integrity. Besides the properties of the cell, working conditions such as the temperature and the discharge rate can also affect the cycle life.

1.8. SPECIFIC TOPICS FOR LITHIUM ION BATTERIES RESEARCH IN PROGRESS

Research opportunities in battery technology, notably lithium batteries, are related largely to the discovery of new or improved electrode and electrolytes through materials design or predictive modelling and to the understanding structure-property relationships and electrochemical behaviour. Key topics include [26]:

- Discovery of new, high-capacity anode and cathode materials which are stable at low/high potentials vs. metallic lithium, respectively, to replace the carbon (e.g., graphite) anodes and the relatively low capacity cathodes of state-of-the-art lithium-ion batteries.
- Identification of new cost-effective electrode and electrolyte materials through theoretical, predictive design.
- Improved electrode design of metal/intermetallic/metalloid anode structures, upon reaction with lithium, can tolerate the significant volumetric expansion so as to improve cycling stability and battery life.
- Nanoscale modification of electrode materials to obtain maximum energy and power without compromising safety.
Tailored surface compositions and structures to improve the stability of the electrode/electrolyte interface.

Identification of additives to enhance the stability of electrode surfaces and prevent overcharging (redox shuttles).

Discovery of new, highly conducting, non-flammable electrolytes to improve safety.

Overall improvement of battery safety through improved materials and designs.

1.9. CATHODES FOR LITHIUM-ION BATTERIES

The cathode is the positive electrode that accepts electrons from the external circuit and is reduced during the electrochemical discharge reaction. The cathode must be an efficient oxidizing agent, be stable when in contact with the electrolyte, and have a useful working voltage. Materials such as metallic oxides are commonly used as cathodes because they can be easily reduced.

Following are the important desirable characteristics of a cathode material:

- High free energy ($\Delta G$) to provide high energy density (high capacity and high voltage)

- Lithium ions should have high diffusion coefficient upon entering into or leaving out of the matrix structure of materials to provide high rate capability and hence, high power density.

- The raw materials used to obtain the final cathode products should be abundant to provide low cost.

- Materials should not react with electrolyte to achieve long cycle life, shelf life and good safety.

- Structural and chemical stabilities during repeatedly charge and discharge processes to provide enhanced cycle life
During the materials optimization and developments, the following designing criterions are often considered:

1) Energy density; 2) Rate capability; 3) Cycling performance; 4) Safety; 5) Cost.

The energy density is determined by the material’s reversible capacity and operating voltage, which is mostly determined by the material intrinsic chemistry such as the effective redox couples and maximum lithium concentration in active materials. For rate capability and cycling performances, electronic and ionic mobilities are key determining factors, though particle morphologies are also an important factor due to the anisotropic nature of the structures and are even playing a crucial role in some cases [27, 28].

*The key requirements for a successful cathode material in a lithium-ion battery are given below [5, 7, 9, 29]:*

- The intercalation cathode \( \text{Li}_x\text{M}_y\text{X}_z \) (\( \text{X} = \text{anion} \)) should have a low lithium chemical potential, and the intercalation anode should have a high lithium chemical potential to maximize the cell voltage. This implies that the transition metal ion \( \text{M}^{n+} \) should have a high oxidation state in the cathode and a low oxidation state in the anode. The chemical potential or redox energies of the cathode and anode could also be tuned by counter cations as illustrated by an increase in voltage on going from an oxide to a polyanion cathode with the same oxidation state for the transition metal ions.

- The intercalation compound should allow for insertion/extraction of a large number of lithium ions per formula unit to maximize cell capacity. This depends on the number of available lithium sites and the accessibility of multiple valence states for \( \text{M} \) in the insertion host.
The lithium insertion/extraction reaction should be reversible, with minimal or no change in structure, leading to good cycle life.

The intercalation compound should support mixed conduction. It should have good electronic conductivity and lithium-ion conductivity to minimize polarization losses during the charge–discharge process, thereby supporting fast charge–discharge rates and power density. The lithium-ion and electronic conductivities depend on the crystal structure, arrangement of the MXₙ polyhedral geometry, interconnection of lithium sites, electronic configuration, and relative positions of the Mⁿ⁺ and Xⁿ⁻ energies.

The redox energies of the cathode and anode should lie within the band gap of the electrolyte. Little variation in unit cell volume during intercalation/deintercalation.

The material reacts with lithium with a high free energy of reaction. (a) High capacity, preferably at least, one lithium per transition metal. (b) High voltage, preferably around 4 V (as limited by stability of electrolyte). This leads to a high-energy storage.

The material should be a good electronic conductor, preferably a metal. (a) This allows for the easy addition or removal of electrons during the electrochemical reaction. (b) This allows for reaction at all contact points between the cathode active material and the electrolyte rather than at ternary contact points between the cathode active material, the electrolyte, and the electronic conductor (such as carbon black). (c) This minimizes the need for inactive conductive diluents, which take away from the overall energy density.

The intercalation compound should be inexpensive, environmentally benign, and thermally and chemically stable.
Regarding these requirements different cathode materials entered into the battery market. The intercalation voltage of the transition metal oxide based cathodes depends on the position of the Mn+/(n+1)+ couple in the electronic structure. During the operation of a lithium-ion cell for topotactic lithium intercalation, the following three main contributions to the energy levels are involved:

- an increase/decrease in the number of electrons in the transition metal electronic bands
- modification of the shape of the bands due to changes in chemical interactions as a result of lithium intercalation
- a change in the electrostatic energy of the material resulting from the change in composition

1.10. RESEARCH TRENDS AND DEVELOPMENT OF CATHODE MATERIALS

1.10.1. 1972-1980: Birth of the cathodes

(a) Intercalation in the layered dichalcogenides

The most extensively investigated insertion materials have a two-dimensional structure; they are MX, MX_2, M_2X_3 compounds with M=In, Ga or V, Ti, Mo, Hf, and X = S, Se and also MPX_3 with M=Fe, Ni, Co, and X=S, Se, Te. These layered materials form alternate structures of covalently bonded layers and van der Waal gaps. Few examples are graphite, TiS_2, MoS_2, MoSe_2, ZrS_2, HfS_2, SnSe_2 and CdI_2 in decreasing order of anisotropy [5, 23, 30].

(b) Trichalcogenides and related materials

The simplest configuration is drain-like tunnels which present essentially one-dimensional migration path for guest ions.
Examples of one-dimensional structure are NbSe$_3$, MoS$_3$, TiS$_3$, and (CH)$_x$ [31].

(c) Movement into oxides

Layered oxides are V$_2$O$_5$, MoO$_3$, LiCrO$_2$, LiCoO$_2$, and LiNiO$_2$. Some insertion compounds have intersecting paths that form a three dimensional array and are referred to as framework compounds. Examples of such insertion compounds are MnO$_2$, WO$_3$, V$_6$O$_{13}$, MoO$_2$, LiMn$_2$O$_4$, and Mo$_6$Sg. Vanadium oxide, V$_2$O$_5$, was one of the first layered oxides studied [32-35]. It has complex intercalation behaviour, involving several phases in relationship with the lithium content. After the first full charge, the lithiated compound shows a sloppy behaviour during galvanostatic cycling. This effect makes V$_2$O$_5$ uninteresting for practical applications. Other vanadium oxide compounds were studied, such as V$_6$O$_{13}$, which can intercalate up to 1 Li per V, and LiV$_3$O$_8$ [8, 36, 37], which structure can be swelled to accommodate more lithium ions. From the viewpoint of applications, cathode materials required for rechargeable lithium cells must possess several desirable properties such as high specific energy, good electrochemical rechargeability, good electronic conductivity, high lithium diffusivity, and chemical compatibility towards the electrolyte.

1.10.2. 1980-1990: Era of layered oxides and first large commercialization

Lithium cobalt oxide (LiCoO$_2$) was the first active material for commercialized positive electrode in large scale lithium ion batteries [7, 8]. The LiCoO$_2$ has a layered structure. The complete removal of the lithium ions from the interslab results structural changes. The oxygen layers rearrange in a hexagonal close packed cell. CoO$_2$ is then electrochemically inactive with respect to Li$^+$ intercalation. Removal of more than 50% of lithium results in an increase of the amount of the irreversible specific charge, without benefit for the reversible specific charge.
LiCoO$_2$ is not the ideal material; it has several and severe disadvantages, related to the safety of the battery, pollution, healthcare, and cost of the cobalt. LiNiO$_2$ has the same structure of the cobalt equivalent, with the advantage of the lower cost of Ni with respect to Co. Studies on this compound suggest an excess of nickel in the structure, localized in the interslab [38]. This disorder causes a reduction of the diffusion coefficient and consequently of the power capability. Moreover, the de-intercalated compound seems to be unstable and therefore dangerous in contact with organic liquids. Many modifications were tried, by substituting part of the nickel with Co or Al [7, 8, 39]. The effect of these additives is to reduce the disorder in the interslab and increase the stability of the structure at low lithium content, respectively, thus bettering the reversibility and the life cycle. Both nickel and cobalt compounds are so called first-generation cathodes for lithium-ion batteries [5].

1.10.3. 1990-2000: Second-Generation of cathodes

Second-generation cathodes materials represent the development of LiNiO$_2$, lithium manganese oxide spinel cathodes (LiMn$_2$O$_4$), layered LiMnO$_2$, and its modifications. An identification and utilization of polyanion compounds, tetrahedral polyanion structure units (XO$_4$)$^{n-}$ (X = P or S) are combined with MO$_6$ (M = transition metal) polyhedral. Due to the strong covalent bonding in (XO$_4$)$^{n-}$, polyanion cathode materials usually possess high thermal stability, which make them more suitable for large-scale energy applications [40-42].

1.10.4. 2000-2010: Third-Generation of cathodes

The layered oxide class Li(Ni$_y$Mn$_z$Co$_{1-y-z}$)O$_2$ is the third generation of active materials for the positive electrode of lithium-ion batteries. The most studied compounds are the ones with $z = y$. In particular, the $z = y = 1/3$ compound was extensively studied.
CHAPTER-I

As general rule, manganese and cobalt are present in the structure as Mn$^{+4}$ and Co$^{+3}$ respectively, while nickel is observed as a mixing of Ni$^{+2}$ and Ni$^{+3}$ [5, 42].

Lithium-excess layered oxides such as $(\text{Li}_2\text{MnO}_3)_x(\text{LiMnO}_2 (M=\text{Ni}, \text{Co}, \text{Mn}))_{1-x}$, offer a $\sim 4.0$ V working voltage with much higher capacity values of $\sim 250$ Ah/kg than those of LiCoO$_2$ and LiMn$_{1.5}$Ni$_{0.5}$O$_2$. However, there is often a huge irreversible capacity loss associated with the oxygen and lithium loss from the host structure of the lithium-excess layered oxides (Li [Li, Mn, Ni, Co] O$_2$) at the end of the first charging process. Although their reversible capacity loss can be significantly reduced by coating with insulating materials (e.g., Al$_2$O$_3$, AlPO$_4$, MgO,RuO$_2$), the high surface area associated with the nanostructured lithium-excess layered oxides (Li[Li, Mn, Ni, Co]O$_2$) could have a high surface reactivity to induce side reactions between the electrodes and the electrolyte. This could lead to destabilization of the active materials and an increase in impeding passivation. Therefore, the electrolyte safety, together with the relatively high cost of the electrode materials, is the major concern for lithium-excess layered oxides to be used as the cathode in LIBs [29].

Borates LiMBO$_3$ have attracted considerable interest as an electrode material, because of its lightest polyanion group, BO$_3$, which ensures higher theoretical energy density than other polyanion cathode materials. Legagneur et al. [43] first investigated the electrochemical properties of LiMBO$_3$ ($M = \text{Mn, Fe, Co}$) compounds. Their results showed that a very small amount of lithium (about 0.04 Li per formula unit) can be deinserted reversibly from the three compounds, i.e. 9 mAh/g, at a rate of C/250 (the theoretical capacity is 220 mAh/g).

1.10.5. 2010-Present: Developments and ongoing research on the cathode materials

Polyanion containing compounds other than LiMPO$_4$ such as Li$_3$M$_2$(PO$_4$)$_3$ ($M = \text{V, Fe or Ti}$), LiVPO$_4$F, Li$_5$V(PO$_4$)$_2$, and LiVOPO$_4$ have also attracted a great deal of interest
in recent years because of their high thermal stability and attractive electrochemical properties [44-50]. Recently, Lithium metal ortho-silicates with general formula \( \text{Li}_2\text{MSiO}_4\), (M=Ni, Mn, Fe, and Co) are another class of the polyanion cathode materials for Li ion batteries. Silicate materials can deliver a theoretical capacity up to 166 mAh g\(^{-1}\) for the extraction of one Li ion and 333 mAh g\(^{-1}\) when two Li ions are extracted [51, 52]. Among the silicate family, \( \text{Li}_2\text{FeSiO}_4\) was the first to be synthesized and was characterized by Nytén et al. in 2005 [53]. \( \text{Li}_2\text{S}\) cathode material exhibits a great potential for the next generation of high performance rechargeable lithium batteries, such as micro batteries for small-size electronic devices emphasizing high charge density, and power sources for electric vehicles. Despite their theoretical promise, elemental sulfur cannot be used directly as an electrode material for lithium batteries at room temperature due to its highly insulating nature and the dissolution of its reaction product polysulfides into the electrolytes, which encountered many serious problems, including low utilization of active material and fast capacity fading [54].

In this regard, Li-ion battery researches, cathode materials attracting the most attention fall into three main crystallographic categories: layered, spinel-type and olivine-type structures. Archetypes are the two-dimensional \( \text{Li}[M]\text{O}_2\) with \( M = \text{Co, Ni, (Ni}_x\text{Co}_{1-x}\) or (Ni, Mn, Co), the three-dimensional \( \text{Li}[X]\text{O}_4\) with \( X = \text{Mn, (Mn}_{1-y/2}\text{Li}_{y/2}\) or (Mn\(_{3/4}\)Ni\(_{1/4}\)) and one-dimensional \( \text{Li}[M']\text{PO}_4\) with \( M' = \text{Fe, Mn, Ni, Co or (Fe}_y\text{Mn}_{1-y}\) [55]. Figure 1.3 illustrates the layer, spinel and olivine structures. The general formula for layered trigonal cathodes can be expressed as \( \text{LiMO}_2\), where M is a 3d transition metal element or a mixture of several 3d transition metals. This structure belongs to the trigonal system with space group \( \overline{\text{R}}\text{3m}\) (166). Oxygen layers form the unit cell frame by stacking along the c-axis in a \( \cdots\text{ABCABC}\cdots\) sequence. Li and M atoms occupy the octahedral interstitial sites between oxygen atoms.
The spinel phases with the general formula LiM₂O₄ (M= transition metal) are also of interest as cathodes in rechargeable Li-ion batteries. Goodenough and his group identified olivine type of positive electrode in general formula of LiMPO₄ (M = Mn, Co, and Ni) as lithium insertion/extraction hosts [31, 42].

![Image of crystal structures of layered, spinel, and olivine phases](image)

**Figure 1.3.** Crystal structure of the three lithium-insertion compounds in which the Li⁺ ions are mobile through the 2-D (layered), 3-D (spinel) and 1-D (olivine) frameworks [55].

### 1.11. IRON-BASED MATERIALS FOR LITHIUM-ION BATTERIES

From many different aspects, iron is a very attractive metal to build large-size batteries for powering electric vehicles or for realizing distributed electrical power sources. Iron is very abundant and eco-friendly benign; it is the fourth most plentiful element in the earth’s crust, being outranked only by Aluminium, Silicon, and Oxygen. It has been the most important metal in the development of civilization to the present time.
Practically, everything that is surrounding us in our life contains iron, or iron based compounds. However, for a sequence of reasons, iron and its derivatives have not met with success as electrode material for lithium-ion batteries. In fact, in the iron-based oxides containing $O^{2-}$ as anion, the Fe$^{4+}$/Fe$^{3+}$ redox energy tends to lie too far below the Fermi energy with respect to a lithium anode, while the Fe$^{3+}$/Fe$^{2+}$ couple is too close to it.

Iron oxide (Fe$_2$O$_3$) was initially tested as an anode for lithium cells. These simple oxide (Fe$_2$O$_3$) of Fe$^{2+/3+}$ couple would normally operate at a voltage of < 2.5 V vs. Li/Li$^+$, surprisingly the polyanion containing Fe$_2$(SO$_4$)$_3$ host was found to exhibit 3.6 V vs Li/Li$^+$, while both Fe$_2$(MoO$_4$)$_3$ and Fe$_2$(WO$_4$)$_3$ were found to operate at 3.0 V vs Li/Li$^+$ (Figure 1.4). The remarkable increase in cell voltage on going from a simple oxide such as Fe$_2$O$_3$ to the polyanion hosts Fe$_2$(XO$_4$)$_3$ and a difference of 0.6 V has been observed between the iso-structural Fe$_2$(SO$_4$)$_3$ and Fe$_2$(MoO$_4$)$_3$ polyanion hosts. All are operating with the same Fe$^{2+/3+}$ couple, which was attributed to an inductive effect and consequent differences in the location of the Fe$^{2+/3+}$ redox levels relative to the Li/Li$^+$ redox level as seen in Figure 1.4[41, 42]. Ohzuku et al. [56] tried to electrochemically insert the lithium into Fe$_2$O$_3$. They found that two lithium equivalents can be introduced into the iron oxide and postulated the formation of FeO and Li$_2$O. In a following work, Pietro et al. [57] prepared Li$_6$FeO$_3$ by Fe$_2$O$_3$ electro reduction. Abraham et al. [58] prepared Li$_6$FeO$_3$ by lithiation of iron oxide with Li-naftalide in THF and tested the so obtained material as anode in Lithium cells. On the other hand, lithiated iron oxides (LiFeO$_2$) were tested as a cathode. LiFeO$_2$ synthesized by high temperature solid-state reaction, can crystallize in three polymorphic modifications: a disordered rock-salt structure, a tetragonal structure and an intermediate combination of the two structures [59]. LiFeO$_2$ with a rock-salt structure synthesized by H$^+$/Li$^+$ ionic-exchange was tested as a cathode.
for Lithium-ion batteries and it was shown that Lithium can be electrochemically removed from the structure [60].

LiFeO$_2$ iso-structural with $\alpha$-NaFeO$_2$ was prepared by a Na$^+$/Li$^+$ ionic-exchange [61] and from a hydrothermal reaction between FeCl$_3$ and LiOH [62]. The electrochemical performance of the prepared materials was not impressive. Corrugated LiFeO$_2$, iso-structural with LiMnO$_2$, was prepared by an ionic-exchange between $\gamma$-FeOOH and LiOH [42]. The material showed a specific capacity of about 100 Ahkg$^{-1}$ and a capacity fade of 1.4 % per cycle. The average discharge voltage was about 2.0 V versus Li.

![Figure 1.4](image.jpg)

**Figure 1.4.** Positions of the Fe$^{2+/3+}$ redox energies relative to that of Li/Li$^+$ in various Fe containing lithium insertion hosts and consequent changes in cell voltages [41].

Kim and Manthiram [63] prepared nanocrystalline lithium iron oxide and studied the lithium intercalation properties of the material. When synthesized by an oxidation
reaction in solution followed by firing the precursors at 200 °C, nanocrystalline iron oxide exhibits capacities as high as 140 Ah kg\(^{-1}\) with an excellent cyclability over a wide voltage range. Other compounds based on iron have been proposed as a cathode for Lithium-ion battery, among them Li\(_2\)FeS\(_2\) [64, 65], FeS\(_2\), FePS\(_3\) [32, 66], FeOCl [67] and FeF\(_3\) [68]. Almost, all these compounds showed poor cyclability, high irreversibility, and low discharge voltage.

1.12. IRON-PHOSPHATES AS CATHODE MATERIALS FOR LITHIUM-ION BATTERIES

The utilization of polyanions such as XO\(_n\)\(^{m-}\) (X = Mo, W, S, P, As) has been shown to lower the Fe\(^{3+}/\)Fe\(^{2+}\) redox energy to useful levels [41, 42]. Monoclinic and hexagonal iron sulphate (Fe\(_2\)(SO\(_4\))\(_3\)) with a NASICON-related framework were synthesized and tested as lithium intercalation hosts [40]. Both forms have been observed a flat discharge voltage of 3.6 V versus Li and a specific capacity of about 100 Ah kg\(^{-1}\). The effect of the structure on the Fe\(^{3+}/\)Fe\(^{2+}\) redox energy of several iron phosphates was studied. Li\(_3\)Fe\(_2\)(PO\(_4\))\(_3\), LiFeP\(_2\)O\(_7\), Fe\(_4\) (P\(_2\)O\(_7\))\(_3\) and LiFePO\(_4\) were investigated by Padhi et al. [40, 41]. Phosphates based materials with high oxidation/reduction potential, such as LiMnPO\(_4\) [69, 70], LiVPO\(_4\)F [71], LiCoPO\(_4\) [72], LiNiPO\(_4\) [73] and multi-electron redox intercalation compounds (Li\(_2\)NaV\(_2\)(PO\(_4\))\(_3\) [74] and Li\(_3\)V\(_2\)(PO\(_4\))\(_3\) [75]).

Iron-based materials offer very promising opportunities for the development of large scale applications for which the cost of materials plays a major role [44]. An overview of Iron-containing phosphates, Silicates, Borates, Fluorophosphates, and Sulfates as positive electrodes in Li-Batteries is shown in Table 1.1. Among these, Lithium iron phosphate (LiFePO\(_4\)) with an olivine structure was investigated as suitable positive-electrode material for rechargeable lithium-ion batteries [41].
Table 1.1. Overview of potential and capacity values of Iron-based phosphates, silicates, borates, fluorophosphates and sulfates positive electrode materials in Li-batteries [44].

<table>
<thead>
<tr>
<th>System Model</th>
<th>Initial/ Final active material</th>
<th>Redox couple</th>
<th>Average potential (V vs Li)</th>
<th>Theoretical capacity (mAh/g)</th>
<th>Energy density (Wh/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NASICON</td>
<td>Fe₂(PO₄)³⁻/Li₂Fe₃(PO₄)⁴⁻</td>
<td>Fe⁺⁺/Fe⁺⁻</td>
<td>3.0</td>
<td>91</td>
<td>273</td>
</tr>
<tr>
<td></td>
<td>Fe₂(WO₄)³⁻/Li₂Fe₂(WO₄)⁴⁻</td>
<td>Fe⁺⁺/Fe⁺⁻</td>
<td>3.0</td>
<td>63</td>
<td>189</td>
</tr>
<tr>
<td></td>
<td>Fe₂(SO₄)³⁻/Li₂Fe₃(SO₄)⁴⁻</td>
<td>Fe⁺⁺/Fe⁺⁻</td>
<td>3.6</td>
<td>134</td>
<td>482</td>
</tr>
<tr>
<td></td>
<td>Li₂Fe₃(PO₄)⁴⁻/Li₂Fe₃(PO₄)⁴⁻</td>
<td>Fe⁺⁺/Fe⁺⁻</td>
<td>2.8</td>
<td>128</td>
<td>358</td>
</tr>
<tr>
<td></td>
<td>LiFe₃(SO₄)³⁻PO₄/Li₂Fe₃(SO₄)⁴⁻PO₄</td>
<td>Fe⁺⁺/Fe⁺⁻</td>
<td>3.3</td>
<td>130</td>
<td>429</td>
</tr>
<tr>
<td>Anti NASICON</td>
<td>Li₂Fe₃(PO₄)⁴⁻/Li₂Fe₃(PO₄)⁴⁻</td>
<td>Fe⁺⁺/Fe⁺⁻</td>
<td>2.88 &amp; 2.73</td>
<td>128</td>
<td>358</td>
</tr>
<tr>
<td></td>
<td>Li₂Fe₃(AsO₄)³⁻/Li₂Fe₃(AsO₄)⁴⁻</td>
<td>Fe⁺⁺/Fe⁺⁻</td>
<td>2.91 &amp; 2.62</td>
<td>98</td>
<td>269</td>
</tr>
<tr>
<td></td>
<td>Fe₂(SO₄)³⁻/Li₂Fe₃(SO₄)⁴⁻</td>
<td>Fe⁺⁺/Fe⁺⁻</td>
<td>3.6</td>
<td>134</td>
<td>482</td>
</tr>
<tr>
<td>Hydrated phosphates</td>
<td>P₂FePO₄·2H₂O/LiFePO₄·2H₂O</td>
<td>Fe⁺⁺/Fe⁺⁻</td>
<td>3.0</td>
<td>157</td>
<td>471</td>
</tr>
<tr>
<td></td>
<td>S·FePO₄·2H₂O/LiFePO₄·2H₂O</td>
<td>Fe⁺⁺/Fe⁺⁻</td>
<td>3.0</td>
<td>157</td>
<td>471</td>
</tr>
<tr>
<td></td>
<td>M·FePO₄·2H₂O/LiFePO₄·2H₂O</td>
<td>Fe⁺⁺/Fe⁺⁻</td>
<td>3.0</td>
<td>157</td>
<td>471</td>
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<tr>
<td>Diposphates &amp; diarsenates</td>
<td>Fe₆P₃O₉³⁻·4H₂O/LiFe₆(P₂O₇)³⁻·4H₂O</td>
<td>Fe⁺⁺/Fe⁺⁻</td>
<td>3.2</td>
<td>131</td>
<td>419</td>
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<tr>
<td></td>
<td>Fe₆(P₂O₇)³⁻/LiFe₆(P₂O₇)³⁻</td>
<td>Fe⁺⁺/Fe⁺⁻</td>
<td>3.1</td>
<td>144</td>
<td>446</td>
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<td></td>
<td>LiFe₆P₃O₉/LiFe₆P₃O₉</td>
<td>Fe⁺⁺/Fe⁺⁻</td>
<td>2.9</td>
<td>151</td>
<td>438</td>
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<td>LiFe₆P₃O₉/LiFe₆P₃O₉</td>
<td>Fe⁺⁺/Fe⁺⁻</td>
<td>3.5</td>
<td>113</td>
<td>395</td>
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<td>LiFe₆P₃O₉/LiFe₆P₃O₉</td>
<td>Fe⁺⁺/Fe⁺⁻</td>
<td>2.55</td>
<td>107</td>
<td>273</td>
</tr>
<tr>
<td>Triphylite, Olshin-type</td>
<td>LiFePO₄/LiFePO₄</td>
<td>Fe⁺⁺/Fe⁺⁻</td>
<td>3.45</td>
<td>170</td>
<td>586</td>
</tr>
<tr>
<td></td>
<td>LiFe₃P₃O₉/LiFe₃P₃O₉</td>
<td>Fe⁺⁺/Fe⁺⁻</td>
<td>3.5 &amp; 2.8</td>
<td>128</td>
<td>590</td>
</tr>
<tr>
<td></td>
<td>LiFe₂SiO₄/LiFe₂SiO₄</td>
<td>Fe⁺⁺/Fe⁺⁻</td>
<td>2.7</td>
<td>165</td>
<td>445</td>
</tr>
<tr>
<td></td>
<td>LiFe₂BO₃/LiFe₂BO₃</td>
<td>Fe⁺⁺/Fe⁺⁻</td>
<td>2.8</td>
<td>219</td>
<td>613</td>
</tr>
<tr>
<td>Tavorite</td>
<td>LiFePO₄·F/LiFePO₄·F</td>
<td>Fe⁺⁺/Fe⁺⁻</td>
<td>2.9</td>
<td>151</td>
<td>438</td>
</tr>
<tr>
<td></td>
<td>Fe₆O₄(OH)₃/LiFe₆O₄(OH)</td>
<td>Fe⁺⁺/Fe⁺⁻</td>
<td>3.25</td>
<td>159</td>
<td>517</td>
</tr>
<tr>
<td></td>
<td>LiFePO₄·(OH)₃/LiFe₆PO₄(OH)</td>
<td>Fe⁺⁺/Fe⁺⁻</td>
<td>2.6</td>
<td>153</td>
<td>398</td>
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<td></td>
<td>LiFe₆O₄·F/LiFe₆O₄·F</td>
<td>Fe⁺⁺/Fe⁺⁻</td>
<td>3.6</td>
<td>151</td>
<td>544</td>
</tr>
<tr>
<td>Triplite</td>
<td>LiFe₅O₄·F/LiFe₅O₄·F</td>
<td>Fe⁺⁺/Fe⁺⁻</td>
<td>3.9</td>
<td>151</td>
<td>589</td>
</tr>
<tr>
<td>Marinite</td>
<td>Li₂Fe₂(SO₄)³⁻/LiFe₂(SO₄)⁴⁻</td>
<td>Fe⁺⁺/Fe⁺⁻</td>
<td>3.83</td>
<td>102</td>
<td>391</td>
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<tr>
<td>Silimanite</td>
<td>LiZn₂Fe₂₃O₅·2F</td>
<td>Fe⁺⁺/Fe⁺⁻</td>
<td>3.60</td>
<td>150</td>
<td>540</td>
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<tr>
<td>KTP</td>
<td>KFe₆PO₄·F/KFe₆PO₄·F</td>
<td>Fe⁺⁺/Fe⁺⁻</td>
<td>3.25, 3.5 &amp; 4.1</td>
<td>128</td>
<td>461</td>
</tr>
<tr>
<td>Layered</td>
<td>LiFeSO₄(OH)·FeSO₄(OH)</td>
<td>Fe⁺⁺/Fe⁺⁻</td>
<td>3.6</td>
<td>151</td>
<td>544</td>
</tr>
</tbody>
</table>
CHAPTER I

1.13. LiFePO$_4$—AN OVERVIEW OF POSITIVE ELECTRODE MATERIALS

LiFePO$_4$ has a practical specific energy as high as 578 Wh kg$^{-1}$. LiFePO$_4$ is a natural product known by the name of Triphylite. The first crystallographic characterization was made by Yakubovich [76] on a sample coming from Palermo Mine, New Hampshire, USA. The compound was correlated to the olivine group. The olivine can be considered as the hexagonal structural analogue of spinel.

In the olivine structure, it is possible to observe two octahedral sites (Fig. 1.5) [77]. Iron is located on octahedral sites and is separated by PO$_4$ bridges. Lithium ions occupy adjacent octahedral sites along the c-axes of a-c planes. LiFePO$_4$ has the ordered olivine structure orthorhombic symmetry. The oxygen atoms are located in a slightly distorted, hexagonal close-packed arrangement. The phosphorus atoms occupy tetrahedral sites; the iron and lithium atoms occupy octahedral 4a and 4c sites, respectively. Each FeO$_6$ octahedron is linked with four FeO$_6$ octahedra through common corners in the b-c plane, forming zigzag planes. The LiO$_6$ octahedra form edge-sharing chains along the b-axis. One FeO$_6$ octahedron has common edges with two LiO$_6$ octahedra. PO$_4$ groups share one edge with an FeO$_6$ octahedron and two edges with LiO$_6$ octahedra as shown in Fig. 1.5.

Lithium can be chemically extracted from LiFePO$_4$ thus leaving a new phase, iron phosphate (FePO$_4$) isostructural with heterosite spatial group of LiFePO$_4$. During lithium extraction, the framework of the ordered olivine is retained with minor displacements. Padhi et al. [41] showed that Lithium can be electrochemically extracted from LiFePO$_4$ and inserted into FePO$_4$ along a flat potential at 3.4 V versus Li. Also, the electrochemical lithium extraction proceeds via a two-phase process and the FePO$_4$ framework of the ordered olivine LiFePO$_4$ is retained with minor adjustments.
The LiFePO$_4$ charge and discharge process can be broadly described as:

\[
\text{LiFePO}_4 \rightleftharpoons \text{Li}_{(1-x)}\text{FePO}_4 + x\text{Li}^+ + x\text{e}^-
\]

LiFePO$_4$ has a theoretical specific capacity of 170 mAh g$^{-1}$. Nevertheless, the electrochemical insertion/extraction of lithium conducted at a specific current as low as 2.1 mA g$^{-1}$ (C/81 rate), was limited to about 0.6 Li per formula unit. A “radial model” for the lithium motion was proposed to explain the poor electrochemical performance of the material [78].

The capacity exhibited from the material was strictly related to the current density used. The observation that the capacity was restored when reducing the discharge current indicates that the loss in capacity was a diffusion-limited phenomenon within a single grain. For this reason, the poor electrochemical material utilization was associated with a diffusion-limited transfer of lithium ions across the two-phase interface.
Galvanostatic intermittent titration technique (GITT) and impedance spectroscopy (IS) were used to calculate the diffusion coefficient of lithium ($D_{Li}$) in $Li_{(1-x)}FePO_4$ as a function of the lithium content. Although, the theory of GITT and IS was shown to be strictly valid for solid solution reactions; Reasonable values for $D_{Li}$ can also be obtained for the case of two-phase reactions if the interaction between the intercalation sites are moderate. The calculated lithium-ion diffusion coefficient in $Li_{(1-x)}FePO_4$ is around $10^{-7}$-$10^{-8}$ cm$^2$ S$^{-1}$ [7, 41, 79], while the actual measure indicating that the diffusion coefficient may be lower than the theoretical value of 7 orders of magnitude ($1.8 \times 10^{-14}$ cm$^2$ S$^{-1}$) [80]. The calculated $D_{Li}$ as a function of x in carbon added $Li_{(1-x)}FePO_4$ was found to be in the range from $1.8 \times 10^{-14}$ to $2.2 \times 10^{-16}$ cm$^2$ S$^{-1}$ for LiFePO$_4$ and FePO$_4$, respectively [7, 19]. LiFePO$_4$ can be considered a mixed ionic/electronic conductor with an electronic band-gap of 0.3 eV. The electronic and ionic conductivities at room temperature are very low, about $10^{-9}$ S cm$^{-1}$ and $10^{-5}$ S cm$^{-1}$, respectively. Therefore, to make LiFePO$_4$ as a suitable cathode material for lithium-ion batteries, its electronic and ionic conductivity must be increased [41, 42].

1.14. IMPLEMENTATIONS OF LiFePO$_4$

In order to overcome the drawbacks of LiFePO$_4$, three strategies were adopted: (i) minimizing particle size via synthesis routes to improve the Li ion diffusivity (ii) carbon coating and dispersing metal powders or metal oxide coating to increase the electronic conductivity; (iii) doping metal ions to increase the intrinsic electronic conductivity. Goodenough’s group first reported LiFePO$_4$ as a cathode material; they prepared it via solid state reaction [41]. Since then, many procedures have been used to prepare LiFePO$_4$ with much better electrochemical properties [30, 42]. The reduction of particles size may have considerable in its advantages kinetics because of the reduced diffusion
pathway length of Li$^+$ [70]. Therefore, reducing the particle size is expected to act on the ionic conductivity owing to the reduction of the diffusion length of the lithium ions in the solid nanocrystalline particles.

The carbon-coating strategy was initially proposed by Armand and co-workers [28], who reported an improvement in the kinetics of the electrochemical reaction after being carbon coating. In general, there are four important functions of carbon coating (i) to act as a reducing agent to avoid formation of trivalent Fe ions during fabrications; (ii) to maintain the particles isolated from each other preventing the consequent undesirable particle growth; and (iii) to enhance the intra and inter-particle’s electronic conductivity; (iv) to avoid the aggregation of nanoparticles and to provide passages for lithium ions. Therefore, reducing the particle size is expected to act on the ionic conductivity owing to the reduction of the diffusion length of the lithium ions in the solid nanocrystalline particles. In contrast, adding a carbon coating should mainly enhance the electronic conductivity [44, 81-86].

Doping ions into LiFePO$_4$ can alter the inherent conductivity effectively. On the basis of different sites, it can be classified as doping at Li (M1) sites, Fe sites (M2) and O sites in LiFePO$_4$ lattice unit. The positive effect of doping on the rate capability and cyclic stability of LiFePO$_4$ has been reported by several groups. Several researchers proposed that the dopants occupied the Li site due to their small ionic radii. Similarly, Fe site doping by small amounts of Na, Cu, Zn, Mg, Ni, Al, Co, Cr, Mn, Ru, Ti, or V also resulted in improved electrochemical properties mainly by enhancing the electronic conductivity. In addition, it has been reported that Fe site doping weakens the Li-O interaction, resulting in high ionic mobility and diffusion co-efficient [87]. Modelling studies also suggested that doping on either Li or Fe sites is energetically unfavourable and does not result in a large increase of electronic conductivity. [88, 89]
Therefore, lattice doping does not appear to be an effective way as surface carbon coating for engineering applications, particularly when taking into account the impact of doping on the cost of raw materials.

1.15. ADVANTAGES & CHALLENGES ASSOCIATED WITH NANOSTRUCTURES OF POSITIVE ELECTRODE MATERIALS

It is well-known fact that nanomaterials have a lot of advantages over their counter bulk materials, especially when are talking about the electrode materials of lithium-based batteries. Nanostructured materials are appealing in this regard, particularly to increase the energy density and rate capability, but there are advantages and disadvantages associated with them. Why the nanomaterials behave differently is explained below, but few disadvantages of nanostructures are also listed here. This enables the readers may pay their attention while developing the nanostructures for lithium battery electrodes. These challenges are easily overcome by good control over structure and fabrication method or by developing hybrid structures [77, 90]. An assortment of anode and cathode materials has been studied for lithium-ion batteries as shown in Figure 1.6.

Some of the advantages…

- The short diffusion length for Li\(^+\) ion transport can enhance the rate capability and power density.
- The high surface area permits a high contact area with the electrode/electrolyte contact area can help to increase the rate capability.
- The smaller particle size aids a better accommodation of the strain during lithium insertion/extraction can help to improve the cycle life.
- The small particle size can aid to realize a better electrochemical utilization of the materials [77].
Some disadvantages…

- The large surface area can lead to enhance the reaction between the electrode surface and electrolyte, resulting in an increase in solid-electrolyte interfacial (SEI) layer area, self discharge and inferior cycle life.

- The low packing density of the particles can lead to lower volumetric energy density.

With these perspectives, nanostructured materials have been pursued as both electrode hosts for lithium ion batteries [7, 19, 77]. Design and development of new materials that can be lower the cost, increase the efficiency and improve the durability. This may have a significant impact in making these technologies commercially viable. In this regard, nanostructured materials and nanotechnology offer great promise, because of...
the unusual properties endowed by confining their dimensions and the combination of bulk and surface properties to the overall behaviour.

One of the most promising issues in electrode material research is the down-sizing of the dimensions. Li-ion transfer can be higher in nanoparticles, rather than in micro-sized particles. Moreover, the enhanced charge transfer improves the rate capability, due to a reduced diffusion/migration-length ratio compared to micrometric-sized particles [91, 92]. Functional electrochemical materials exhibit two effects at the nano-scale, i.e., an intrinsic effect due to the extra ionic defects of the space charges in the nano particles, and an extrinsic effect due to an increased diffusion of ions on surfaces regions with enhanced defect diffusion pathways.

1.16. MANUFACTURING DESIGN CRITERIA OF Li-ION CELLS

There are four different configurations of lithium ion batteries that can be found in the current market i.e. cylindrical, coin, thin/flat polymer and prismatic battery configurations (Figure 1.7) [3]. Among these, in the earlier days, cylindrical cell configuration (Figure 1.7a) has been used as common design for lithium ion batteries. Within the cylinder, all components could be soaked in liquid electrolyte; positive electrode, separator, and current collectors could be rolled around the central cylindrical negative electrode, usually made of carbon. This design saved spaces and maximized the capacity so that it has been one of the most popular cell configurations in the market, especially for primary cell batteries [15].

In order to meet the requirement of portable electronics, such as watches, remote controller, and calculators, etc., smaller, thinner, and lighter design of coin cell (Figure 1.7b) has been developed. This cell can contain anode, separator, and cathode, which were lying from bottom to top and were soaking in liquid electrolyte [93].
In 1999, polymer electrolytes replaced the liquid electrolyte in secondary lithium ion batteries, which eliminated the shape restriction of cylindrical cell [15].

A thin film polymer battery (Figure 1.7 c & d), with numerous advantages including shape versatility, flexibility, and lightness, which was consisting anode current collector, anode, polymer electrolyte, cathode, and cathode collector (a schematic is shown in Figure 1.7 (c & d)). Each part of a thin film lithium ion polymer battery is a thin membrane; some thin film batteries are less than 0.3 mm thick [94, 95].

**Figure 1.7** Lithium battery has very high design flexibility to be fabricated into different shapes: a. cylindrical, b. coin, c. prismatic, and d. thin and flat. Courtesy form [9]
1.17. POSTULATE IN ELECTROCHEMICAL PROPERTIES OF BATTERIES

1.17.1. Calculation of the Capacity of Electrode Materials

Theoretical Capacity

The theoretical capacity of an electrode reaction calculated in Ampere hour per gram (Ah/g) can be maximized with an increased electron transfer/equivalent weight of active material ratio as seen in the following equation.

Theoretical capacity =

\[
\frac{\text{Number of electron transferred}}{g / \text{mole (active material)}} \times \left( \frac{96485 \text{ C}}{\text{mole}} \times \frac{1 \text{ A.S}}{1 \text{ C}} \times \frac{1 \text{ hr}}{3600 \text{ s}} \right) = \frac{\text{Ah}}{g}
\]

The terms in brackets can be condensed to a constant of 26.8 Ah/mole. Charge and discharge capacity is also a measure of energy density (Wh/L) in watt hour per liter (i.e. (Wh/L) = V× Ah/L) and also referred to as specific energy (Wh/kg) = V× Ah/kg.

Rate Capability

Rate capability is an another parameter to evaluate electrode performance. The term charge/discharge rate (or) C-rate is often used to describe how fast the cell can be charged or discharged; C denotes either the theoretical charge capacity of a cell or battery (mAh) or the nominal capacity of a cell or battery as indicated by the manufacturer.

Irreversible Capacity Loss

It is also important to define how much capacity is lost after each cycle. Then irreversible capacity can reflect the stability of cells upon cycling. Irreversible capacity loss is explained by following equation

For anode

\[
\text{I.C.L} = \frac{n_{Qd} - n_{Qc}}{n_{Qd}} \times 100 \%
\]
For cathode

\[ \text{I.C.L} = \frac{n_{Qd} - n_{Qc}}{n_{Qc}} \times 100\% \]

When \( n \) is the number of cycles for the charge/discharge test, \( Q_d \) is the specific discharge capacity and \( Q_c \) is the specific charge capacity for each cycle.

**Capacity Retention**

Capacity Retention is the ratio of the last cycle to the first cycle discharge capacity. It is calculated as a percentage and calculated by the given relation,

\[ \text{Capacity Retention} = \left( \frac{C_n}{C_1} \right) \times 100\% \]

where, \( C \) is the discharge capacity, \( C_1 \) is the initial discharge capacity, \( n \) is the number of cycle.

**Coulombic Efficiency**

Coulombic efficiency (C.E) is defined as the ratio of the discharge capacity to the charge capacity, expressed in percentage.

\[ \text{C.E} = \left( \frac{n_{Qd}}{n_{Qc}} \right) \times 100\% \]

Lower efficiency \( \text{C.E} < 1 \) implies an unwanted side reaction or electrolyte reaction occurring during the electrochemical charge.

**Electrochemical principles of Li-Ion Batteries**

There are three different kinetics plays a major role for the overall polarization, which can be seen in Figure 1.8. At first, the activation polarization is related to the kinetics if the charge-transfer reactions are taking place at the electrode/electrolyte interface. The ohmic polarization can be attributed to the resistance of the individual cell components and to the resistance due to contact problems between the cell components. Finally, the concentration polarization is due to mass transport limitations during cell operations.
Figure 1.8 also illustrates the current-voltage characteristics on discharge, a common electrochemical technique to determine the cell capacity, the effect of the discharge/charge rate and general information on the state of the battery.

![Diagram of battery discharge characteristics]

**Figure 1.8.** A typical discharge curve of a battery, showing the influence of different types of polarization, adopted from Winter & Linden et al. [3, 26].

The losses that can be seen in Figure 1.8 are to be avoided when minimizing the polarization losses, the following guidelines are important and to be followed for all batteries [3, 26].

- An electrolyte with a lower conductivity will give a higher ohmic polarization.
- The electrolyte, including both salts and solvents, should be chemically stable within the cell range to avoid unwanted reactions with the electrode materials.
- The activation polarization can be reduced by increasing the rate of electrode reaction at both anode and cathode. A porous electrode design will give a high electrode surface and thus minimize the charge-transfer polarization.
• The cell should have adequate electrolyte transport to facilitate the mass transfer, and thus avoid building up an excessive concentration polarization. In the most battery systems, the reactants must diffuse or be transported away from the electrode surface. Porosity, pore size, separator properties and concentration of the reactants influence the mass transfer.

• The current collectors should be compatible with the electrode material and the electrolyte and should not cause corrosion problems.

• The reaction products should facilitate the reversible reactions during charge and discharge, as well as being mechanically and chemically stable with the electrolyte.

**C rate:** C rate is used to indicate the charge and discharge currents for a battery cell. Manufacturers specify the rates for cells they develop as an indication of feasible operating rates without damaging the cells. A discharge rate of 1C means that the current delivered by the battery will discharge the battery in one hour. If a greater discharge rate is used, the time to discharge the battery will be shorter, i.e. one (1) divided by the C rate (in hours). When choosing a battery it is important to decide at what discharge and charge currents will be used, so that the battery usage will manage the currents for the system and the charger.

\[ h = \frac{1}{C} \]

where, \( h \) represents the time in hours for discharging at the rate C. For example, discharging a battery with the capacity of 20 Ah, at 1C will discharge the battery with a constant current of 20 A. The total discharge time will then be 1 hour. If using a C-rate of 5C for the same battery, the constant current will be 100 A with a discharge time of 1/5 h, i.e. 12 minutes.
**Concentration polarization:** Concentration polarization is the most dominant factor contributing to the battery cell voltage drop of the mass diffusion phenomenon. The concentration polarization is what occurs at the electrodes due to the different velocity of the ions depending on what distance these are from the electrode. The charges (ions) diffuse in the flux gradient to reach the equilibrium state. By that the charges depletes the region close to the electrode from charges due to the larger flux gradient in the nearby surroundings of the electrode. Leaving the area further away from the electrode more concentrated with charges a concentration difference will appear. The flux gradient increases with increased current supplied to the load, which leads to that the concentration difference of charges also increases. If no current is supplied to the load, the natural state of the battery contains a certain concentration of charges in the area close to the electrodes due to diffusion. Now, when current is supplied to the load the concentration of charges around the electrodes will drop as mentioned. When this concentration of charges is so reduced that it is lower than in the natural state, a voltage drop will occur. Higher rates of charging and discharging the battery cell leads to a higher voltage drop due to the higher flux gradient that depletes the region closer to the electrode from charges faster.

1.17.2. Cell thermodynamics

**Thermodynamic parameters in cells**

Assuming the cell is in thermodynamic equilibrium, including zero charge exchange, the open-circuit voltage (OCV) \( V (i = 0) \) can be measured. It does not depend on the direction of reaction [7]. According to the first and second laws of thermodynamics, the system has energy

\[
\Delta E = \Delta Q + W = T\Delta S - P\Delta V + W_e \tag{1.1}
\]
where T, S, P and V are temperature, entropy, pressure, and volume of the system, respectively, and \( W_e \) is the electrical work that the cell can provide.

Therefore,

\[
W_e = \Delta E - T \Delta S + P \Delta V = \Delta G
\]  

1.2)

The Gibbs free energy \( \Delta G \) represents the maximum amount of work, and can be extracted from an open-circuit measurement of potential V,

\[
\Delta G = W_{\text{max}} = -nFV
\]

1.3)

where \( n = 1 \) for Li\(^+\)/Li pair and F is the Faraday constant of a mole of charge. \( F = eN_A = 96485 \) C (or 26.8 Ah) and \( N_A \) is the Avogadro constant. From Eq. 1.3, the chemical potential change \( \mu \) can be obtained

\[
\mu = \frac{\partial G}{\partial n} \bigg|_T
\]

\[
\mu = -eV
\]

1.4)

Assuming dP = 0, and replacing molar fraction by a composition \( x = n/N_A \), it gives

\[
dG = -FVdx - SdT
\]

1.5)

With Maxwell relations, this yields

\[
\frac{\partial S}{\partial S} \bigg|_T = F \frac{\partial V}{\partial T} \bigg|_x
\]

1.6)

\[
\frac{\partial H}{\partial x} \bigg|_T = -FV + T \frac{\partial^2}{\partial x} \bigg|_T = -FV + TF \frac{\partial V}{\partial T} \bigg|_x
\]

1.7)

Equations 1.6 and 1.7 relate basic thermodynamic functions to electrochemical parameters. For example, a change of the entropy difference between the two electrodes with Li\(^+\) concentration is proportional to the change of how the open-circuit voltage depends on temperature at a fixed state of charge.
Gibbs phase rule in cells

The Gibbs phase rule of thermodynamics can be applied to battery cells provided the system is under thermodynamic equilibrium. The number of degrees of freedom \( f \) is given by

\[
f = c - p + 2
\]

(1.8)

where \( c \) is the number of components and \( p \) is the number of coexisting phases. Most often, the lithium intercalation in the electrode is a two-component system \((c = 2)\), the \( \text{Li}^+ \) ions and the host structure. Therefore, if giving a single phase \((p = 1)\), besides temperature \((T)\) and pressure \((P)\), there is only one more degree of freedom \((f = 3)\). Thus the chemical potential \( \mu \) (or OCV) has to be a function of \( T \), \( P \), and composition \( x \). In the case of a two phase mixture, there is no more independent degree of freedom besides \( T \) and \( P \) (\( f = 2 \)), so all thermodynamic functions such as \( \mu \), \( S \), or \( H \) should remain constant with composition \( x \) under a fixed \( T \) and \( P \).

1.17.3. Cell kinetics

Arrhenius relation

It was Arrhenius who first found that general reaction kinetics have exponential dependence on \( 1/T \) and proposed the form

\[
k = k_0 \exp(-E_a/k_B T)
\]

(1.9)

where \( E_a \) is usually called the activation energy, or standard internal energy of activation. It has a difference of \( \Delta PV \) compared to the standard enthalpy of activation, \( \Delta H \) (i.e., they become the same when \( \Delta PV \) is ignored), \( k_0 \) is the attempt frequency factor. This prefactor can also be included in the product \( k'_0 \exp\Delta S/k_B \), which involves the standard entropy of activation, \( \Delta S \). Thus the Arrhenius equation (Eq. 1.9) can be recast as

\[
k = k'_0 \exp(-\Delta G/k_B T)
\]
where $\Delta G$ is the standard Gibbs free energy of activation [8]. Equation 1.10 is an equivalent statement of Eq. 1.9, an empirical interpretation of reaction kinetics.

**Nernst equation and Tafel equation on electrodes**

For an electrode reaction, equilibrium is described by the Nernst equation,

$$E = E_0 + \frac{RT}{nF} \ln \left( \frac{C_o}{C_r} \right)$$

(1.11)

where $C_o$ and $C_r$ are bulk concentrations of the cathodic and anodic components in the electrode. This equation says that if all steps have facile kinetics and are chemically reversible, the electrode potential and the surface concentrations of the initial reactant and final product are in local Nernstian balance at all times, regardless of the current flow [8]. Many systems satisfy these conditions. The dependence of current on potential is often complicated. As for overpotential, one empirical relation is known as Tafel equation:

$$\eta = a + b \log i$$

(1.12)

where $\eta$ is the overpotential, difference between the actual potential and thermodynamically determined reduction potential.

**Marcus theory of electron transfer**

The field of electron transfer has been developed quickly since 1940s. Compared to many other chemical reactions, the electron transfer process happens fast, without breaking and forming chemical bonds. The earliest experimental observations were explained by the Franck-Condon principle, which is used widely to interpret excitation spectra of vibronic quantum states. According to this principle, the nuclear coordinates must actuate into a suitable configuration from the reactant to the product.

Marcus proposed that the potential energy curves for the reactant and the product intersect, and with the electronic coupling, charge transfer happens in a radiation less, or
iso-energetic way. Let \( q \) be the reaction coordinate. The free energies of the reactant \( R \) and product \( P \) depend quadratically on the reaction coordinate:

\[
\begin{align*}
GR(q) &= \frac{k}{2}(q - q_R)^2 \\
GP(q) &= \frac{k}{2}(q - q_P)^2 + \Delta G
\end{align*}
\]  

(1.13)

(1.14)

where \( q_R \) and \( q_P \) are the coordinates for the reactant and product in equilibrium, and \( k \) is a proportionality constant (e.g., a force constant for changing the bond length). \( \Delta G \) is the free energy difference between \( R \) and \( P \) under their equilibrium conditions. According to the Franck-Condon principle, charge transfer occurs only at the intersection of free energy curves of \( R \) and \( P \), where the nuclear coordinate becomes \( q^* \).

The free energies at the transition state are

\[
\begin{align*}
GR(q^*) &= \frac{k}{2}(q^* - q_R)^2 \\
GP(q^*) &= \frac{k}{2}(q^* - q_P)^2 + \Delta G
\end{align*}
\]  

(1.15)

(1.16)

Since \( GR(q^*) = GP(q^*) \), \( q^* \) can be solved

\[
q^* = \frac{(q_R + q_P)}{2} + \frac{\Delta G}{k} \frac{q_P - q_R}{(q_P - q_R)^2}
\]

(1.17)

the free energy of activation for the reaction from \( R \) to \( P \) relative to \( GR(q_R) \) is given by

\[
\Delta G^*_r = GR(q^*) = \left( \frac{\lambda}{4} \right) \left( 1 + \frac{\Delta G}{\lambda} \right)^2
\]

(1.18)

where \( \lambda = \frac{k}{2} (q_P - q_R)^2 \) is the critical parameter called the reorganization energy, representing the energy needed to transfer the nuclear configurations in the reactant to those of the product state.

**Fick’s laws**

Mass transfer to an electrode is governed by the Nernst-Planck equation, in addition to Fick’s first law of diffusion,

\[
J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{\Sigma_i F}{RT} \frac{\partial N(x)}{\partial x} + \frac{\partial F_i(x)}{\partial x} + \frac{\partial C_i(x)}{\partial x}
\]

(1.19)

where \( J_i(x) \) and \( C_i(x) \) are the flux (mol.s\(^{-1}\).cm\(^{-2}\)) and concentration of species \( i \) at distance \( x \) from the surface, \( D_i \) is the diffusion coefficient (cm\(^2\)/s), \( \partial C_i(x)/\partial x \) is the concentration
gradient at $x$, and $\partial \phi(x)/\partial x$ is the potential gradient. The three terms represent contributions to the flux from diffusion, migration, and convection, respectively [9]. The Einstein relation is derived from Fick's first law, when only diffusion is considered,

$$\text{(1.20)}$$

where $u$ is the ionic mobility, $z$ is the number of charges per unit, and $F$ is the Faraday constant. The Einstein relation connects the diffusion coefficient $D$ and ionic mobility $u$.

Since molar conductivity $\sigma = z \cdot u \cdot F$, from Eq. 1.20, we have

$$\text{(1.21)}$$

as the general expression for conductivity. In the case of a strong electrolyte, the conductivity $\sigma$ is the sum of contributions of cations and anions,

$$\sigma = \mu_+ \sigma_+ + \mu_- \sigma_- \quad \text{(1.22)}$$

where $\mu_+$ and $\mu_-$ are the number of cations and anions. For time-dependent diffusion processes, Fick's second law gives

$$\frac{\partial C_i(x)}{\partial t} = D_i \frac{\partial^2 C_i(x)}{\partial x^2} \quad \text{(1.23)}$$

1.18. THERMODYNAMIC AND KINETIC ASPECTS

Conduction in Lithium Ion Batteries

The overpotential of an electrochemical reaction depends on several processes, and all of them can be rated limiting steps during charge and discharge of a LIB electrode. In summary, these include: i) Solid state diffusion of lithium towards the particle surface (or into the particle), ii) Surface kinetics of lithium (de-)intercalation, iii) Electric conduction through the conductive carbon network, iv) Ionic conduction (migration) and v) Diffusion through the liquid phase (electrolyte) in the electrode pores. For the production of high power electrodes, the contribution of conduction processes can be kept small by i) increasing the amount of conductive carbon, ii) reducing the size of
active particles and iii) using thinner electrode films and iv) utilizing highly conducting, low viscosity electrolytes. The question major is that, which type of conduction is the most rate limiting, is often difficult to answer. Advanced electroanalytical techniques such as current interrupt (CI) or electrochemical impedance spectroscopy (EIS) are therefore required to determine the inner resistance of the battery [96].

1.19. LITERATURE SURVEY

In this part, the reviews of recent progress of LiFePO$_4$ cathode materials via polyol technique and surface modification of LiFePO$_4$ using metal oxide/ carbonaceous materials were described.

1.19.1. Preparation methods

During the past years, several novel synthesis approaches had been developed for lithium iron phosphate with a small crystallite size as well as good electrochemical performances. The overview of preparation of LFP has been divided into two main categories: Solid-state synthesis and solution-based synthesis. Solid-state synthesis is the most “robust” and conventional method used industrially to synthesize powder materials for lithium batteries because of its (apparent) simplicity, ideal for continuous large-scale production. Solution-based syntheses are more versatile, with the possible use of a large panel of solvents: aqueous, classical organic, polyols, or, from quite recent reports, ionic liquids. This segment will give a “particular” overview of the polyol technique from the early beginning until today.

**Polyol process**

Kim et al. [97] reported that the LiFePO$_4$ nanoparticles were prepared from the polyol medium of Fe-acetate [Fe-(CH$_3$COO)$_2$], ammonium dihydrogen phosphate (NH$_4$H$_2$PO$_4$), and Li-acetate (Li-CH$_3$COO) by refluxing them at 335°C for 16 h. The sample showed orthorhombic shape with an average width of 20 nm and a length of 40
nm with a monodispersed state and high crystallinity. The XRD pattern was indexed on the basis of an orthorhombic olivine structure type (space group: $Pnma$). The LiFePO$_4$ sample showed an initial capacity of 166 mAh/g at a current density of 0.1 mA/cm$^2$, which amounts to a utilization efficiency of 98%. In the cyclability test, the LiFePO$_4$ showed a reversible capacity of 166 mAh/g in the first cycle and approximately 163 mAh/g from the 2nd to 50th cycle. Especially, it exhibited an excellent rate performance at high current rates of 30 or 60 C by providing around 58 and 47% of capacity retentions, respectively. The reaction temperature was changed to vary the particle growth. The solution was heated slowly up to 200 °C and then rapidly heated to 320 °C with a 10 min time interval. The temperature of the solution was kept at 320 °C for 16 h [98]. The particles consisted of various shapes like nanorod and nanoplate with an average size of 300 and 100 nm respectively. The initial discharge curve of LiFePO$_4$ capacity showed 168 mAh/g highly at the 0.1C rate with well-formed plateau in the voltage range of 2.5-4 V.

Sinha et al. [99] reported that the nanoplate LiFePO$_4$ could be synthesized by a polyol route starting from two simple reactants, namely, FePO$_4$ and LiOH. The crystalline compound was formed by refluxing a tetraethylene glycol solution consisting of FePO$_4$ and LiOH at 335°C without further heating of the reaction product. The nanoplates have average dimensions of 30 nm width and 160 nm length, as measured from transmission electron micrographs. The surface area of the LiFePO$_4$ sample is 38 m$^2$g$^{-1}$. Also, the sample is porous with broadly distributed pores around 50 nm. The discharge capacity values were measured as 160 and 100 mAh g$^{-1}$ at 0.15 and 3.45 C, respectively. A stable capacity of about 155 mAh g$^{-1}$ was obtained at 0.2 C over a 50 charge-discharge cycle.
Lim et al. [100] synthesized the LiMPO$_4$ (M = Fe, Mn, Co) nanocrystals via solvothermal method using the polyol medium of DEG, transition metal acetates [M-(CH$_3$COO)$_2$] (M = Fe, Mn, Co), phosphoric acid (H$_3$PO$_4$) and lithium acetate (Li-CH$_3$COO) in a Teflon-lined stainless steel bomb at 200–240 °C for 16 h.

Singh et al. [101] synthesized LiFePO$_4$ rhombohedral particles with orthorhombic crystal structure by polyol process from iron nitrate and lithium dihydrogen phosphate salts in diethylene glycol solvent without any post heat treatment. The solution was refluxed by heating at temperature 245 °C for 6 and 18 h. They studied the carbon and MWCNTs coated on the surface of LiFePO$_4$. The initial discharge capacities of LiFePO$_4$, MWCNT/LiFePO$_4$ composites and Carbon coated LiFePO$_4$ (C/LiFePO$_4$) rhombohedral particles were observed as 68 and 84 mAh/g, 104 and 115 mAh/g and 91 and 146 mAh/g at a current rate of 0.1 C in the potential range 2-4.2 V under room temperature and 40 °C, respectively.

Lim et al. [102, 103] described the synthesis of olivine structured LiFePO$_4$ samples via solvothermal process by employing various polyol media of ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), and tetraethylene glycol (TTEG) without any further heating as a post procedure. The samples prepared using EG, DEG, TEG, and TTEG showed the reversible capacity of 118, 167, 90, and 105 mAh/g respectively at current density of 0.1 mA/cm$^2$. Among these samples, the samples based on DEG and TTEG showed good performances at high rate of 16 C with high capacity retention. Highly nanocrystalline LiFePO$_4$ was synthesized by solvothermal process in a polyol medium namely, diethylene glycol (DEG) without any heat-treatment as a post procedure by Lim et al. [104, 105]. Nanoplate LiFePO$_4$ indicated initial discharge capacity of 138 mAh/g and exhibited stable capacity retention until 50 cycles.
Azib et al. [106] prepared LiFePO$_4$ nanoplatelets via polyol process by varying the synthesis conditions, viz the solvent and the metal precursor concentration.

Mathew et al. [107] prepared nano-structured LiFePO$_4$ by simple polyol refluxing process using Fe-oxy-acetate (Fe(OH)(CH$_3$COO)$_2$), phosphoric acid (H$_3$PO$_4$), lithium acetate and tetraethylene glycol (TTEG) as a polyol medium. The reaction was performed at heat rate 15 °C/min and maintained at 320 °C by varying the reaction time (1, 4, 8, 16 and 32 h) viz. When this sample was performed charge/discharge analysis and exhibited discharge capacities of 161, 162, 171, 143 and 155 mAh$^{-1}$, respectively for the reaction time 1, 4, 8, 16 and 32 h.

Li et al. [108] reported that the LFP/C composites have been synthesized from a low-cost divalent Fe-containing precursor by polyol process in a relative short reaction time. The LiFePO$_4$/C showed an excellent rate capability and cycle performance, with initial discharge capacities of 153, 128, and 106 mAh g$^{-1}$ at 1, 5 and 10 C respectively. The capacity retention is respectively 98.7, 98.2, and 98.7 %, after 10 cycles at the corresponding rates. The capacity retention remains at 97 % even after 300 cycles at 10 C rate. Nanoscale LiFePO$_4$/C cathode with highly crystalline characteristics was prepared directly by a rapid polyol-assisted pyrosynthetic technique, performed in open-air.

1.19.2. Metal oxide modified LiFePO$_4$

Metal oxide modification is one of the approaches to enhance the electrochemical performances of LiFePO$_4$ cathode material. Nowadays, different metal oxides have been widely used to coat the cathode materials, for example, suppressing transition metal dissolution, preventing direct contact between cathode and electrolyte, stabilizing cathode material structures, and so on.
Hu et al. [109] reported that the nanometer-sized RuO$_2$ can repair the incomplete carbon network as well as improve the kinetics and rate capability of the composite significantly. Le´on et al. [110] precipitated ZnO films with a thickness of 2 nm on the surface of LiFePO$_4$/C particles and obtained a significantly enhanced capacity retention at different rates.

Chang et al. [111] synthesized TiO$_2$ coated LFP using sol-gel process and the effects of the oxide coating on the high-temperature (55 °C) cycle performance of LiFePO$_4$-based cells were also studied. The results indicated that the presence of the TiO$_2$ coating helps to reduce the Fe dissolution at the cathode.

Liu et al. [112] found that the surface modification of LiFePO$_4$ with ZrO$_2$ could greatly enhance the cycle ability. The capacity of the coated LiFePO$_4$ electrode remained at 143.4 mAh g$^{-1}$ after 100 cycles at 0.1 C rate, which was higher than that of the uncoated sample (138 mAh g$^{-1}$).

Liu et al. [113] reported that the electrochemical properties of CeO$_2$ modified LiFePO$_4$ electrodes were improved when compared to the pristine LiFePO$_4$ electrode. CuO and carbon co-coated LiFePO$_4$ was reported by Cui et al. [114]. Their studies revealed that the co-coating reduced the capacity fading and the interfacial resistances and the polarization of the cathode.

Cui et al. [115] enhanced the properties of ZnO and carbon co-coated LFP particles made by sol-gel and freeze drying processes. The ZnO/C co-coated LFP composites showed high exchange current density ($i^o$) which enhanced the electrochemical performance in terms of rate performance and capacity. Zhang [116] observed that the charge transfer between particle surface and current collector plays a crucial role on the high-rate performance of LiFePO$_4$. 

47
Li et al. [117] proposed that SiO$_2$ coated LiFePO$_4$/C, effectively enhances the cycling capacity and reduces capacity fading at high temperature and alleviates the cell impedance. This is attributed to the presence of SiO$_2$ on the particle surface which effectively prevents the LiFePO$_4$ particles from the direct contact with the electrolyte solution. This improved the structural stability, reduced the interfacial resistance and thereby increased the Li-ion conductivity.

Jin et al. [118] reported the performance of V$_2$O$_3$ modified LiFePO$_4$/C materials by solid state reaction method. The prepared materials exhibits better electrochemical performance in rate capability and low temperature behaviour, and the presence of V$_2$O$_3$ improved the apparent lithium ion diffusion coefficient of LiFePO$_4$/C.

Zhao et al. [119] analyzed Al$_2$O$_3$-coated LiFePO$_4$ powder prepared by sol-gel method. The discharge capacities of the uncoated LiFePO$_4$ were ~150 mAh g$^{-1}$ at 0.1 C and 110 mAh g$^{-1}$ at 5 C, whereas the capacity of the 2 wt. % coated LiFePO$_4$ cell were nearly 155 mAh g$^{-1}$ at 0.1 C and 123 mAh g$^{-1}$ at 5 C.

Yao et al. [120] investigated the effect of CeO$_2$ coating on LiFePO$_4$/C cathode material prepared by sol-gel process. The CeO$_2$-coated LiFePO$_4$/C cathode material showed an improvement in lithium insertion/extraction capacity and electrode kinetics, especially at high rates and at low temperature. At -20 °C, the CeO$_2$-coated material delivered discharge capacity of 99.7 mAh/g at 0.1C rate and the capacity retention of 98.6% was obtained after 30 cycles at various charge/discharge rates.

LFP/(C+CdO) particles synthesized by spray-drying process followed by heat-treatment, which is favourable to enhance the conductivity of LFP/C and LFP/(C+CdO) samples, which were studied by Yang et al. [121]. It may be an efficient barrier to prevent the direct contact between LFP particles and electrolyte solution, thus eliminating
Fe dissolution in the electrolyte and improving the structural stability of LiFePO₄. The initial discharge capacity of both electrodes showed no obvious difference (i.e., 161.9 and 164.2 mAh g⁻¹ for LFP/C and LFP/(C+CdO)). LFP/ZnO/Carbon composites were prepared by vibratory wet ball milling of ZnO, Polyethylene glycol (PEG) and LFP particles via solid state method by Lee et al. [122].

Ziolkowska et al. [123] analysed the successful use of low cost sol-gel method to synthesize pure and Sn-modified LiFePO₄. Reduced material degradation during charging/discharging cycling and excellent lithium intercalation reversibility in Sn-modified LiFePO₄ was attributed to a positive surface modification effect of the SnO₂ layer. The specific discharge capacity of pure LiFePO₄ is 101 mAh g⁻¹, while the Sn containing samples had significantly higher capacities: 122, 122 and 114 mAh g⁻¹ for samples LFP:Sn (1:99), LFP:Sn (3:97) and LFP: Sn (5:95), respectively. Liu and Wang reported [124] the first attempt of conducting metal oxide that was made WO₂ to modify LiFePO₄/C particles via in-situ synthesis method.

Liu et al. [125] synthesized MoO₂ and carbon co-coated LiFePO₄ cathode materials by a combined technique of solid state synthesis and the sol-gel method. Also, MoO₂ modified LiFePO₄/C cathode materials had been synthesized via in situ synthesis method by Liu et al. [126]

Quan et al. [127] prepared LiFePO₄/C/CoPO₄ composites using hydrothermal method (in situ method). The key roles of CePO₄ nanoparticles had been summarized into two aspects: First, nail effects: Introducing CePO₄ with in situ method during the synthesis process can reduce particle size and combine LiFePO₄ particles, making stronger connections to buffer the volume change; Second, protection effects: CePO₄ nanoparticles, as ionic conductor with stable structure in electrolytes, can protect electrodes from the corrosion of electrolytes like pre-formed SEI.
Chen and Mao [128] observed that the reduced titanium oxide $\text{Ti}_3\text{O}_5$ powder would replace acetylene black as the conductive additive for $\text{LiFePO}_4$ cathode in lithium-ion cells. First discharging of the cathode with $\text{Ti}_3\text{O}_5$ powder keeps the capacity of 170.9, 150.8, 134.6 and 107 mAh g$^{-1}$ at 0.1, 0.5, 1 and 2 C, respectively.

1.19.3. Surface modification of LFP via carbonaceous materials

Conductive additive is an important part of the Lithium Ion Batteries and facilitates the transport for both lithium ions and electrons. To date, commonly studied cathode materials are semiconductors or insulators. In this aspect, the conductive additives are required not only for good ionic and electrical conductivities, but also for capability to absorb and retain the electrolyte and hold the active material to restrict their volumetric changes. Among these, conductive additives, the nanocarboneous materials have been playing a significant role in the surface development of LFP cathode materials for high-rate Lithium-ion batteries.

**Carbon coating**

Huang et al. [129] reported that $\text{LiFePO}_4$/C released nearly 120 mAh/g at 5 C rate when 20 wt. % carbon black was used. Chen and Dahn [130] reported that the discharge capacity of $\text{LiFePO}_4$/C was 110 mAh/g at 2 C rate when the carbon content was 7 wt. %.

Zaghib et al. [131] reported the electrochemical performance of natural graphite-fibers /polyethylene oxide (PEO) - based gel electrolyte/$\text{LiFePO}_4$ batteries. A different approach has been reported by Bhuvaneswari et al. [132] based on the addition of functionalized carbon nanofibers (two-dimensional system (CNFs)) during the sol-gel synthesis of $\text{LiFePO}_4$. Park et al. [133] added carbon black into the precursor to enhance the conductivity of $\text{LiFePO}_4$. 
MWCNT coated LFP

Whittingham et al. [134] indicated that the addition of MWCNTs in the hydrothermal preparation of LiFePO₄ enhanced the electronic conductivity of the final product. Li et al. [135] demonstrated that LiFePO₄/MWCNTs composite cathode displayed a initial discharge capacity of 155 mAh/g at 0.1 C rate and a gradual decrease in discharge capacity upon cycling was also observed by them.

Muraliganth et al. [136] proposed a novel microwave-solvothermal approach to produce single-crystalline LiFePO₄ nanorods and LiFePO₄-MWCNT nanocomposites without requiring elevated temperature, post processing in reducing gas atmospheres. They suggested that short nanorod of LiFePO₄/MWCNT nanocomposite showed better rate performance than long nanorod of LiFePO₄/MWCNT nanocomposite. The shorter LiFePO₄ nanorods exhibited higher discharge capacity at a given C-rate than the longer nanorods owing to a faster lithium ion diffusion due to the shorter diffusion length.

Zhou et al. [137] enlightened that a well crystalline LiFePO₄ with 3D network was appealing since it can provide fast electronic conduction in the solid phase and ion conduction at reasonable rates in both solid and liquid phases and maximize energy storage per geometric area.

Wu et al. [138] analysed crystalline LiFePO₄ nanoplates, which was incorporated with 5 wt. % multi-walled carbon nanotubes (CNTs) via facile low temperature polyol process in one single step without any post heat treatment. They observed a reversible specific capacity of 155 mAh g⁻¹ at the current rate of 10 mA g⁻¹ and capacity retention ratio close to 100 % after 100 cycles.

Nanosize C/LiFePO₄/MWCNTs composite particles were synthesized by a combination of hydrothermal progress and a facile electro-polymerization polyaniline
process with simultaneous calcinations by Qin et al. [139]. The C/LiFePO$_4$/MWCNTs composites exhibited a better rate performance with a capacity of 169.9, 153.3, 151.5 and 143.4 mAh/g at 0.1, 5, 10 and 20 C rates, respectively.

**Graphene coated LFP**

As graphene is extendable in two dimensions, it can easily tether active materials particles onto its surface. Thus, graphene can be explored as an excellent conductive substrate for numerous application fields, among which the energy application is the most intensive and interesting one [140]. Graphene serves as an excellent conducting supporter for battery materials. Integrating graphene has been explored as simple but extremely effective route towards high performance phosphate electrodes [141].

Yu et al. [142] prepared the thermally exfoliated graphene oxide (TEGO) and in-situ microwave exfoliated graphene oxide (MEGO) coated LFP materials. LiFePO$_4$/MEGO exhibited polarization of 53.3 mV and delivered specific capacity of 158.1 mAh g$^{-1}$ at 0.1 C, resulting in better specific energy of 518.1 Wh kg$^{-1}$ with the energy efficiency of 89.8%. Even at the high rate i.e., 10 C, LiFePO$_4$/MEGO had a polarization of 618.5 mV and specific capacity of 104.3 mAh g$^{-1}$, corresponding to an excellent specific energy of 300.3 Wh kg$^{-1}$. After 2000 cycles, the LiFePO$_4$/MEGO still performed excellent rate capabilities with 91.2% retention.

Tian et al. [143] synthesized olivine-type LiFePO$_4$/graphene composite materials through high temperature solid-state method. LiFePO$_4$/graphene (92:8 wt.) cathode delivered a capacity of 167 mAh g$^{-1}$ at 0.1 C and could tolerate various discharge currents with a capacity decay rate of just 27.2 %, after cycled stepwise at 0.1, 2, 5 C for 15 times, respectively.
Kim et al. [144] reported a novel method for the fabrication of micro-sized and porous graphene embedded LiFePO$_4$ by 3D assembly of LiFePO$_4$ primary nanoparticles with graphene sheets using stable amide bonds between them induced by a catalyst.

Hu et al. [145] reported that the carbon-coated lithium iron phosphate, surface-modified with 2 wt. % of the electrochemically exfoliated graphene layers, was able to reach 208 mAh g$^{-1}$ in specific capacity. The excess capacity was attributed to the reversible reduction-oxidation reaction between the lithium ions of the electrolyte and the exfoliated graphene flakes, where the graphene flakes exhibited a capacity higher than 2,000 mAh g$^{-1}$.

Yang et al. [146] described the use of unfolded graphene as a three dimensional (3D) conducting network for LiFePO$_4$ nanoparticle growth. Compared with stacked graphene, which has a wrinkled structure; the use of unfolded graphene enables better dispersion of LiFePO$_4$ and restricts the LiFePO$_4$ particle size at the nanoscale. LiFePO$_4$-unfolded and stacked graphene nanocomposites achieved a discharge capacity of 166.2 and 77 mAh g$^{-1}$ during the 1$^{st}$ cycle.

Wu et al. [147] reported that the LFP nanoparticles loaded on graphene (G) with sucrose (S) as a linker (G-S-LFP). 5 wt.% G-S-LFP exhibited an excellent rate capability with an initial discharge capacities of 165 (0.5 C), 151 (1 C), 146 (2 C), 133 (5 C), and 115 mAh g$^{-1}$ (10 C), whereas 2 wt.% G-S-LFP showed a corresponding capacities of 144 (0.5 C), 126 (1 C), 120 (2 C), 106 (5 C), and 93 mAh g$^{-1}$.

Toprakci et al. [148] synthesized LiFePO$_4$/C and LiFePO$_4$/graphene/C composite nanofibers using electro spinning, followed by heat treatment. The initial reversible capacities were 150, 162, and 165 mAh g$^{-1}$, respectively, for pristine, LiFePO$_4$/C and LiFePO$_4$/graphene/C composite nanofibers.
LiFePO$_4$/graphene composites could be synthesized via polyol route [149], hydrothermal route [150], solvothermal route [151], sol–gel route [152], and so on.

Zhou et al. [153] created a 3D network of graphene wrapping on the LiFePO$_4$ particles via hydrothermal method. The graphene sheets were bridged into a 3D conductive network, which was supported the maximum fulfilment of its function because electrons could be easily transferred between the particles and graphene. The results indicated that this kind of graphene modification could give rise to an excellent rate performance.

Ding et al. [154] investigated the effect of graphene on LiFePO$_4$, which was synthesized by co-precipitation. However, no significant improvement in the electrochemical performance was observed, when compared the conventional carbon coating. In this case, LiFePO$_4$ particles were loosely loaded on the graphene sheets.

Nagaraju et al. [155] studied about a three dimensionally wrapped conductive thin sheets of GO along with the LiFePO$_4$ using aqueous GO solution and LiFePO$_4$ precursors. It exhibited a discharge capacity of 161 mAh/g at C/10 rate and excellent cycling stability.

Sung Hoon Ha and Yun Jung Lee [156] synthesized carbon coated core-shell structured LiFePO$_4$ (LFP/C-rGO) via in-situ polymerization method. The LFP/C-rGO cathode reached a discharge capacity of 168 mAh/g at a slow rate of 0.05 C and still delivers a capacity of 72 mAh/g at 60 C.
1.20. SCOPE OF THE INVESTIGATION

The lithium iron phosphate (LiFePO$_4$) is an attractive suitable positive electrode material among the other olivine compounds and layered oxides. To ensure the safety, high energy batteries must be very stable under normal conditions and adverse environments such as high temperatures and overcharged conditions. Consequently, LiFePO$_4$ is the most thermally and electrochemically stable material. Considering that the rate performances of the materials are technically easy to improve, LiFePO$_4$ was chosen as a candidate to study on and to improve its rate capability.

Also, it offers a variety of advantages such as eco-friendly, high safety, low cost, high theoretical capacity, high energy density and high operating voltage. However, an intrinsic drawback of this material is its low electronic/ionic conductivity, which can be conquered by reducing the particle size and/or coating with an electronically conductive material (surface modification of LiFePO$_4$) via low cost, energy-efficient low temperature polyol technique.

The primary challenge of our study on LiFePO$_4$ was to explore and compare various synthesis conditions and to characterize the resulting materials as a function of their structural, physicochemical, and electrochemical properties. In order to increase the electronic conductivity of the composites, several strategies have been adopted such as optimization of synthetic procedures, carbon nano-coating, particle size minimization, metal powder addition, doping with supervalent ions, and carbothermal formation of the surface conducting phase. Keeping these aspects in view, in the present study, an attempt has been made to optimize and develop the simple preparation procedure to improve low electronic conductivity and cycling performance of LiFePO$_4$. 
The specific research goals were the following:

- To prepare LiFePO$_4$ cathode material via binary precursor using polyol technique and without any post heat treatment and special environment. The low boiling point diethylene glycol (DEG) has been used as a polyol solvent for the entire investigations. The prepared material is going to be compared with the other methods like hydrothermal and solid state reaction.

- An attempt has been made to prepare metal oxide tailored LiFePO$_4$ composite cathode materials via modified polyol process. In this study, three kind of metal oxide has been used namely NiO, CeO$_2$ and Nb$_2$O$_5$.

- To develop the rate performance and specific capacity of LiFePO$_4$, a carbonaceous coating has been made on the core materials via polyol process. Oxalic acid, MWCNTs and graphene are used for carbonaceous materials.

- To characterize the structural, morphological, elemental and magnetic performance through XRD, FT-IR, Raman spectrum, FE-SEM with EDX, HR-TEM with SAED, XPS and VSM.

- To fabricate the coin cell and study the electrochemical performance using charge/discharge, cyclic life, CV, rate performance and impedance spectra under room temperature.
REFERENCES


CHAPTER-I


