Among various energy storage technologies, rechargeable lithium-ion batteries have been considered as effective solution to the increasing need for high-energy density electrochemical power sources. Rechargeable lithium-ion batteries offer energy densities 2 - 3 times and power densities 5 - 6 times higher than conventional Ni-Cd and Ni-MH batteries, and as a result, they weigh less and take less space for a given energy delivery. However, the use of lithium-ion batteries in many large applications such as electric vehicles and storage devices for future power grids is hindered by the poor thermal stability, relatively high toxicity, and high cost of lithium cobalt oxide (LiCoO$_2$) powders, which are currently used as the cathode material in commercial lithium-ion batteries. Recently, lithium iron phosphate (LiFePO$_4$) powders have become a favorable cathode material for lithium-ion batteries because of their low cost, high discharge potential (around 3.4 V versus Li/Li$^+$), large specific capacity (170 mAh g$^{-1}$), good thermal stability, and high abundance with the environmentally benign and safe nature. As a result, there is a huge demand for the production of high-performance LiFePO$_4$. However, LiFePO$_4$ also has its own limitation such as low conductivity ($\sim 10^{-9}$ S cm$^{-1}$), which results in poor rate capability. To address this problem, various approaches can be used such as decreasing particle size of LiFePO$_4$, doping LiFePO$_4$ with metal ions or coating LiFePO$_4$ surface with carbaceous materials. Formation of conductive layer on LiFePO$_4$ and decreasing particle size are promising approaches due to their superior contribution to electrical conductivity and electrochemical performance of LiFePO$_4$. Although different approaches can be used for surface coating and particle size
decrement, electrospinning can be potentially considered as an efficient, simple and inexpensive way. In this study, LiFePO₄/carbon and carbon nanotube- and graphene-loaded electrospun LiFePO₄/carbon composite nanofibers were synthesized by using a combination of sol-gel and electrospinning. During the material preparation, polyacrylonitrile (PAN) was used as an electrospinning media and a carbon source. LiFePO₄ precursor materials and/or conductive materials (carbon nanotubes and graphene) and PAN were dissolved in N,N-dimethylformamide separately and they were mixed before electrospinning. LiFePO₄ precursor/PAN fibers were heat treated, during which LiFePO₄ precursor transformed to energy-storage LiFePO₄ material and PAN was converted to carbon. The surface morphology, microstructure and electrochemical performance of the materials were analyzed. Compared with conventional powder based positive electrodes, the novel LiFePO₄/C composite nanofiber cathodes possess better electrochemical performance. Furthermore, the newly developed LiFePO₄/C composite nanofibers are easy to fabricate, highly controllable, and can be used in practical Lithium-ion battery applications.

In addition to LiFePO₄, more recent efforts have been directed to mixed form of layered lithium metal oxides (Li-Ni-Mn-Co). Nickel and manganese are of importance because of their lower cost, safety and higher abundance in nature. These new cathodes offer noticeable improvement in the capacity and cycling behavior. In these cathodes, LiNi₁/₃Co₁/₃Mn₁/₃O₂ attracted significant interest because of its good electrochemical properties such as high capacity, prolonged cycling life, and so on. On the other hand, it has some disadvantages such as instability at high voltages and high current densities. To overcome these problems, synthesis of layered Li-rich composite materials such as xLi₂MnO₃·(1-x)LiCo₁/₃Ni₁/₃Mn₁/₃O₂ can be a promising approach. In this study, various xLi₂MnO₃·(1-x)LiCo₁/₃Ni₁/₃Mn₁/₃O₂
(x=0.1, 0.2, 0.3, 0.4, 0.5) composite cathode materials were prepared by a one-step sol-gel route. Morphology, microstructure and electrochemical behavior of these cathode materials were evaluated. The resultant cathode material shows good electrochemical performance. Relatively low cost and simple preparation route make new xLi$_2$MnO$_3$·(1-x)LiMn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$O$_2$ composite materials possible to use as potential cathode candidate for lithium-ion batteries.
Advanced Nanofiber-Based Lithium-Ion Battery Cathodes

by
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DEDICATION

To my mother, father, sister and wonderful wife Aylin, without whose love, guidance and support, this would not have been possible.
BIOGRAPHY

Ozan Toprakci was born on June 28th, 1982 to Zaide and Ibrahim Toprakci of Denizli, Turkey. He graduated from Denizli Science High School in July of 1999. He attended Ege University in September 1999, and graduated with a Bachelor of Science in Textile Engineering in July 2004. After graduation, he obtained a shift manager position in Abalioglu Spinning Mill Co., Ltd., where he did two years of work as a shift manager.

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CHAPTER 1. INTRODUCTION

1.1. Overview of electrospinning

The synthesis and fabrication of one-dimensional (1D) nanostructures with a variety of forms, such as nanotubes, nanowires, nanobelts, and nanofibers, have gained intensive attention in recent years due to their extraordinary properties and intriguing applications in many areas including tissue engineering, catalysis, sensors, biomedicine, filtration, reaction materials, electrochemical electrodes, affinity membranes, nano-composites, etc. There are various ways to produce nanofibers such as, drawing,\(^1\) template synthesis,\(^2, 3\) phase separation,\(^4\) self-assembly,\(^5, 6\) or electrospinning (Figure 1.1). Among these techniques, continuous and long nanofibers can be produced effectively via electrospinning.

Electrospinning is a simple process that creates nanofibers from polymer solution or polymer melt by using electrostatic force. By this process, a nonwoven web with ultrafine fibers having diameters in the range of a few nanometers to a few microns can be produced. Electrospinning is an old technique which is firstly observed by Rayleigh in 1897. Although, the first setup using the electrospinning technology was patented by Formhals\(^7\) in 1934, it has come into prominence in last 15 years.
Figure 1.1. Common nanofiber production techniques: (a) drawing, (b) self-assembly, (c) template synthesis, and (d) phase separation.

Electrospinning process (Figure 1.2) usually consists of a syringe fitted in a metered pump, a high voltage (10-60 kV) power supply to charge the polymer solution, and a
grounded collector plate separated by certain distance to deposit the fiber web. In the process, electrical potential is applied between a capillary tube and a collector plate. By the effect of electrical force, hemispherical shape of the droplet at the end of the capillary tube turns into a conical shape, known as Taylor cone. When the applied electrical force overcomes to the surface tension of the droplet, charged jet of polymer solution is ejected from the tip of Taylor cone. As this jet travels in the air, it is accelerated by the electrical force, partially or fully solidified through solvent evaporation and then collected as nanofiber mats on the metal collector (Figure 1.2 inset). Fiber formation is extremely rapid process (in $10^{-3}$ s) and fiber elongation ratio is extremely huge (around $10^5$-$10^6$). These values are not accessible with conventional fiber production methods, such as fiber extrusion followed by mechanical stretching.

Figure 1.2. Schematic illustration of the conventional set-up for electrospinning.
1.2. Applications of electrospun nanofibers

In recent years, there has been a strong interest in developing new applications for electrospun nanofibers due to their unique properties including long length, high porosity, and high surface area. As proposed by Reneker et al.,\textsuperscript{9} electrospun nanofibers can be used as reinforcing fibers in composite materials, wound dressing materials, non-wetting surface layer on ordinary textiles, or polymeric separation membranes.

Electrospun nanofibers can be used as supporting materials for catalysts. Electrospun TiO\(_2\), ZnO\(_2\), and SnO\(_2\) nanofiber mats are strong substrates for loading many metal nanostructures (such as Pt, Rh, or Pd) used in catalytic applications.\textsuperscript{11} Due to their large surface area, metal-coated electrospun nanofibers exhibits enhanced catalytic ability for a number of reactions. Therefore, electrospun TiO\(_2\) nanofibers can be directly used as photocatalyst for hydrogen evoluation due to their semi-conductive nature.\textsuperscript{12}

Electrospun nanofiber membranes have superior capability to remove small particules from air or aqueous solutions. They are widely used as filters due to their macroporous structures.\textsuperscript{13} Fe\(_2\)O\(_3\), SnO\(_2\), TiO\(_2\), and ZnO loaded nanofibers or metal-oxide ceramic nanofibers can also be used as gas sensors to detect NO\(_2\), CO, O\(_2\), H\(_2\), CH\(_3\)OH, etc.\textsuperscript{14-16}

One-dimensional characteristics of electrospun nanofibers make them attractive candidates for energy conversion/storage devices including solar cells. Electrospun carbon nanofibers (CNFs) can be used as electrode supports for fuell cells. Pt or Pt-Pd alloy
nanoparticles supported by CNFs are used in direct methanol fuel cells and show improved electrocatalytic ability.\textsuperscript{17} Electrospun TiO$_2$ nanofiber membranes are used in dye-synthesized solar cells as photoelectrodes.\textsuperscript{18, 19}

Electrospun nanofibers have also been explored as anodes, cathodes or separators in lithium-ion batteries.\textsuperscript{20} Ji et al. used CNFs, metal oxide/carbon and metal/carbon composite nanofibers as binder-free anodes for rechargeable lithium-ion batteries (LIBs).\textsuperscript{21-29} Electrospun polyvinylidene fluoride nanofibers are used as polymer electrolyte membranes\textsuperscript{30, 31} or separators\textsuperscript{32} for LIBs.\textsuperscript{31} Electrospun LiCoO$_2$,\textsuperscript{33} LiNiO$_2$,\textsuperscript{34} and LiFePO$_4$/C\textsuperscript{35, 36} composite nanofibers were also produced as positive electrodes for rechargeable LIBs (Figure 1.3). As shown in Figure 1.4, Chen et al.\textsuperscript{37} produced LiCoO$_2$/C nanofibers from electrospun LiCoO$_2$ precursor/polyvinylpyrrolidone (PVP) composite nanofibers.

![Figure 1.3](image)

**Figure 1.3.** The schematic diagrams of (a) active material, (b) active material-carbon complex, and (c) electron transfer pathway of active material/carbon nanofiber\textsuperscript{35}
1.3. Overview of batteries

A battery is a device that converts the chemical energy contained in its active materials directly into electric energy by means of an electrochemical oxidation-reduction (redox) reaction. Today, it is believed that the first modern electric battery was invented by Alessandro Volta in 1800. According to archeological findings of Wilhelm König in 1938 (near Baghdad, Iraq), battery has a possible history goes back to 248 BC.\textsuperscript{38, 39} These findings and their schematic presentation is shown in Figure 1.5.
While the term “battery” is often used, the basic electrochemical unit being referred to is the “cell”. A cell is the basic electrochemical unit providing a source of electrical energy by direct conversion of chemical energy. The cell consists of an assembly of electrodes, separator, electrolyte, container and terminals. A battery consists of one or more electrochemical cells, electrically connected in an appropriate series/parallel arrangement to provide the required operating voltage and current levels, including, if any, monitors, controls and other ancillary components (*i.e.* fuses, diodes), case, terminals and markings. The cell consists of three major components:

- The anode or negative electrode, *i.e.* the reducing or fuel electrode, which gives up electrons to the external circuit and is oxidized during the charging.
- The cathode or positive electrode, *i.e.* the oxidizing electrode, which accepts electrons from the external circuit and is reduced during charging.

- The electrolyte, the ionic conductor, which provides the medium for transfer of charge, as ions, inside the cell between the anode and cathode. The electrolyte is typically a liquid, such as water or other solvents, with dissolved salts, acids, or alkalis to impart ionic conductivity. Some batteries use solid electrolytes, which are ionic conductors at the operating temperature.

In most batteries, porous structure is of great importance. A sponge-like electrode will have high discharge current and capacity, and a porous separator between the electrodes can effectively stop the short circuit, but allow the exchange of ions freely.\textsuperscript{42} Electrochemical operation of a cell is shown in Figure 1.6.

![Electrochemical operation and internal construction of a typical cell.](image)
1.3.1. Classification of batteries

Batteries available in the market are usually classified as primary and secondary batteries in terms of their reusabilities.

1.3.1.1. Primary batteries

Primary batteries, irreversibly (within limits of practicality), transform chemical energy to electrical energy. When the initial supply of reactants is exhausted, energy cannot be readily restored to the battery by electrical means. The following are some common primary lithium batteries:

- Lithium/sulfur dioxide (Li/SO₂) batteries
- Lithium/thionyl chloride (Li/SOCl₂) batteries
- Lithium/manganese dioxide (Li/MnO₂) batteries
- Lithium/carbon monofluoride (Li/CF₃) batteries

1.3.1.2. Secondary batteries

Secondary batteries can have their chemical reactions reversed by supplying electrical energy, restoring their original composition. Carbon-zinc, rechargeable alkaline, lead-acid,
lithium-ion, lithium-ion polymer, lithium-sulfur, molten salt, nickel-cadmium, nickel-iron, nickel hydrogen, nickel-zinc, sodium-sulfur, zinc-bromine flow batteries are some of secondary batteries. As shown in Figure 1.7, lithium-ion batteries have the 40% share of the battery market. In the last decade, production volume of lithium-ion batteries increased more than 2 times. According to energy experts, the production will increase 10 times more in the following 20 years to accommodate energy necessities of next generation.

1.4. Overview of lithium-ion batteries

Lithium is an alkali metal with silver-white appearance, soft handle, low density (0.534 g cm$^{-3}$), large specific capacity (3860 Ah kg$^{-1}$), low electrochemical potential, high electronegativity, and high energy density.$^{46, 47}$ As an alkali metal, lithium is highly reactive, and hence it is found in nature as compounds that can be used for different applications, such as pharmacology, aerospace, construction, and energy storage. Lithium-ion batteries get their name from the lithium ion that moves from the anode to the cathode during discharging and from the cathode to the anode during charging. This characteristic is shown in Figure 1.9.
Figure 1.7. (a) Total battery production statistics in 2010 and (b) growth of lithium-ion battery industry since 2000 (Original data supplied by the Battery Association of Japan)
Rechargeable lithium-ion batteries, which are based on lithium chemistry and were first commercialized by Sony in 1992, are of importance as new generation power sources because they are lighter and have higher energy density, lower self discharge, no memory effect, prolonged service-life, larger number of charge/discharge cycles, better environmental friendliness, and higher safety when compared to many other battery systems. Hence, lithium-ion batteries are being widely used for portable electronics from digital cameras to notebooks and music players to cell phones (Figure 1.8). They are also potential systems for large-scale applications, such as electric vehicles and storage devices for future power grids, if they can be produced with lower cost, smaller sizes, lighter weights, and higher energy storage capacities.

A standard lithium-ion battery consists of anode, cathode and electrolyte, as shown in Figure 1.9. When the battery is charged, lithium ions deintercalate from the cathode and intercalate into the anode through the electrolyte; while on the discharging process, lithium ions deintercalate from the anode and intercalate into the cathode. During charge/discharge cycles, electrons flow between the anode and the cathode, enabling the conversion of chemical energy and also the storage of electrochemical energy within the battery. Therefore, the performance of a rechargeable lithium-ion battery strongly depends on the active materials employed in both the anode and cathode for lithium storage.
The common materials for anodes are carbon, lithium-alloying metals, graphite varieties (such as modified natural graphite or kish graphite), and carbon nanotubes/nanofibers. The most used cathode material is LiCoO$_2$, which is currently being used in commercial lithium-ion batteries found in portable electronic devices such as laptops and cell phones. However, the high cost, poor thermal stability at elevated temperatures and high toxicity of LiCoO$_2$ make it an unsuitable material for larger-scale applications. Therefore, battery manufacturers have turned to find other alternative materials to replace LiCoO$_2$, and examples of such materials include layered lithium nickel oxide (LiNiO$_2$), lithium manganese spinels (LiMn$_2$O$_4$), vanadium oxides (LiV$_3$O$_8$), and olivines (LiMPO$_4$, M = Fe, Co, Mn or Ni). Common anode and cathode materials used in lithium-ion batteries are briefly given in Chapter 1.4 and 1.5, respectively.
1.4.1. Anode materials for lithium-ion batteries

Shukla et al.\textsuperscript{49} reported that most common anode materials were carbon-based materials, lithium-alloying metals, and their composites. Carbon-based anodes exhibit good chemical and thermal stability, excellent mechanical stress tolerance (ductility), good electronic and ionic conductivities, and also considerable Li-storage ability. Carbon matrix is used as the host for Li-alloying metals and some transition metal oxides, to buffer the large volume change resulting from repeated lithium insertion and extraction. These materials are given in the following chapter, briefly.
1.4.1.1. Carbonaceous anodes

The carbon materials have demonstrated lower initial irreversible capacities, higher cycle-ability and faster mobility of Li in the solid phase. The carbon-based electrodes were developed to eliminate problems of lithium metal deposition. On charge, lithium metal electrodes deposit “moss-like” or “dendrite-like” metallic lithium on the surface of the anode. Once such metallic lithium is deposited, the battery is vulnerable to internal shorting, which may cause dangerous thermal run away. The use of carbonaceous material as the anode active material can prevent such dangerous phenomenon. There are various types of carbon materials which can be used as anodes in Li-ion batteries including highly oriented pyrolytic graphite (HOPG), natural graphite, artificial graphite, hard carbons, mesophase low temperature fibers and mesocarbon microbeads (MCMB).\(^5\)\(^1\) Figure 1.10 presents a scheme of major classes of carbons, which are currently studied in connection with Li-ion battery systems.

1.4.1.2. Novel graphite varieties

Shukla et al.\(^4\)\(^9\) reported about new modified natural graphites and other graphitic carbons such as kish graphites. The air oxidation of natural graphites results in kish graphites with improved electrochemical properties. Kish graphites have lithium intercalation capacities
well above 372 mAh g\(^{-1}\) and their production costs are inexpensive compared with other synthetic graphitic anodes.

Figure 1.10. Schematic representation of various types of carbons.\(^{43}\)

1.4.1.3. Carbon nanotubes (CNTs)

There are several classifications of CNTs. According to configuration, they can be divided into armchair, zigzag, and chiral; according to degree of graphitization, they can be divided into amorphous and graphitic. Or according to structure, they can be divided into single wall (SWCNTs) and multi wall carbon nanotubes (MWCNTs).\(^{52}\) The latter
classification can be seen in Figure 1.10. As reported by Shukla et al.\textsuperscript{49} MWCNTs are high-capacity anodes for lithium storage but their irreversible capacities are too large. CNTs also have high charge-discharge rates, high electrical and thermal conductivities, and high tensile and shear strength. To minimize irreversible changes, CNT anodes can be used with lithium-alloying metals as composites.

1.4.1.4. Silicon

While graphite is a weak material, meaning that it can only absorb a certain amount of ions, it can be repeatedly charged and discharged without significant issues. Silicon alternatives, on the other hand, tend to swell when charged and shrink when discharged, resulting in stress fractures. These make traditional silicon alternatives impractical for use after several charge/drain cycles.\textsuperscript{53} Miller et al.\textsuperscript{54} reported that Li-Si composites provide an opportunity to improve the performance and safety of these batteries while reducing cost. Theoretical capacity of Si is more than 4000 mAh g\textsuperscript{-1}, and this value is larger than the theoretical capacity of graphite. On the other hand, one drawback of these materials is the significant expansion that occurs in the Si host during Li alloying (>300%). The repeated expansion/contraction of the lattice during cycling degrades the Si structure, severely limiting cycle life. These characteristics can be seen from the Figure 1.11. The sample with low Si content demonstrated extremely stable cycling characteristics (more than 400 cycles), but the
capacity is limited to 125 mAh g$^{-1}$. The sample containing the higher Si content shows improved capacity (>250 mAh g$^{-1}$), but the cycle life was limited to 70 cycles. In addition, the poor electrical conductivity of silicon (only 2.5 S cm$^{-1}$) leads to heat generation upon cycling due to the high internal resistance and limits the applicable charge current. The enhanced cyclability of these materials can be attributed to a high degree of dispersion of the elemental Si within the nanocomposite structure.

Figure 1.11. Comparison of capacity versus cycle life for Si-based nanocomposite anodes produced by high impact ball milling.$^{54}$

Wolf et al.$^{55}$ reported that the 3D-carbon fiber substrate containing graphite was coated with nanosized silicon by using atmospheric microwave plasma. As seen from Figure 1.12, longer coating time leads to larger silicon particles. Figure 1.13 shows that the carbon–silicon-composites are clearly superior compared to the carbonaceous substrate up to a
silicon content of 34 wt%. Reversible specific capacity is more than 1200 mAh g$^{-1}$ for the 34 wt% sample.$^{55}$

Figure 1.12. SEM-images of three carbon/silicon composites, prepared with different coating time. Coating time: (a) 1 min, (b) 2.5 min, and (c) 5 min.$^{55}$

Figure 1.13. First cycle reversible and irreversible specific capacity in dependence of silicon content at a charge/discharge current of 0.05 C.$^{55}$
1.4.1.5. Alloy anodes

Many alloy systems have been studied as anode materials for secondary lithium batteries. It has been observed that metallic anodes are able to form lithium alloys offering capacities superior to those of the carbon based systems (370 mAh g\(^{-1}\) for the theoretical LiC\(_6\)); however a severe problem is usually related to the formation and decomposition of a lithium alloy; \(i.e.,\) an impressive volume change. This change leads to mechanical stresses on the anode which may induce cracks and rapidly disintegration of the electrode. The cycle life of the lithium alloy anode is therefore severely decreased and these electrodes usually offer only a few cycles before their capacity fades. This problem has been significantly improved by synthesizing intermetallic MM’ alloys with active (M) and inactive (M’) elements or by ultrafine alloy powder. It is aimed to produce smaller sized particles to reduce the extent of local volume change during cycling. Chen \textit{et al.}\(^{58}\) showed these crack formation in Ni–Sn alloy during lithiation process as Figure 1.14.

Brousse \textit{et al.}\(^{57}\) reported that two advantages of the metal oxides as anodes can be envisioned: one is that the metal obtained after decomposition of metal oxide is embedded in a lithium oxide matrix which seems to help the metal to accommodate the volume change during the formation and decomposition of the alloy; and the second advantage is that the metal particles formed from the decomposition of the oxide can be very small and thus less likely to fracture. They also showed irreversible and reversible theoretical capacities of
thermodynamically possible metal oxides in Table 1.1. In the table, the most promising elements for anodes were marked with “*”.

Figure 1.14. Schematic of the crack formation in Ni–Sn alloy during lithiation (a) initial film structure, (b) lithiation of excess Sn in the surface causing some plastic deformation of the substrate, (c) decomposition of Ni$_3$Sn$_4$ and further lithiation of the Sn and plastic deformation of the copper and (d) fracture on delithiation.$^{58}$

Song et al.$^{59}$ produced melt-spun Al$_{0.6-x}$Si$_{0.4}$Mn$_x$ (x = 0, 0.01, 0.03, 0.05, 0.07 and 0.1) alloys. A high-specific capacity (more than 500mAh g$^{-1}$) and a stable cycling performance (90% capacity retention) have been achieved in melt-spun Al$_{0.55}$Si$_{0.40}$Mn$_{0.05}$ and Al$_{0.52}$Si$_{0.40}$Mn$_{0.07}$ alloys after 10 cycles. This phenomenon was shown in Figure 1.15.$^{59}$
Table 1.1. Theoretical irreversible and reversible capacities calculated for some metal oxides.\textsuperscript{57}

<table>
<thead>
<tr>
<th>Elements</th>
<th>Li richest alloy</th>
<th>Oxide</th>
<th>$Q_{\text{irrev}}$ mAh g\textsuperscript{-1}</th>
<th>$Q_{\text{rev}}$ mAh g\textsuperscript{-1}</th>
<th>$Q_{\text{rev}} / Q_{\text{irrev}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al*</td>
<td>Li$_9$Al$_4$</td>
<td>Al$_2$O$_3$</td>
<td>1577</td>
<td>1183</td>
<td>0.8</td>
</tr>
<tr>
<td>Si*</td>
<td>Li$_{22}$Si$_5$</td>
<td>SiO$_2$</td>
<td>1785</td>
<td>1963</td>
<td>1.1</td>
</tr>
<tr>
<td>Zn*</td>
<td>LiZn</td>
<td>ZnO</td>
<td>659</td>
<td>329</td>
<td>0.5</td>
</tr>
<tr>
<td>Ag*</td>
<td>Li$_{12}$Ag</td>
<td>Ag$_2$O</td>
<td>167</td>
<td>2000</td>
<td>12</td>
</tr>
<tr>
<td>Ga</td>
<td>Li$_2$Ga</td>
<td>Ga$_2$O$_3$</td>
<td>858</td>
<td>572</td>
<td>0.7</td>
</tr>
<tr>
<td>Ge</td>
<td>Li$_{22}$Ge$_5$</td>
<td>GeO$_2$</td>
<td>1025</td>
<td>1128</td>
<td>1.1</td>
</tr>
<tr>
<td>As</td>
<td>Li$_3$As</td>
<td>As$_2$O$_3$</td>
<td>813</td>
<td>813</td>
<td>1.0</td>
</tr>
<tr>
<td>Se</td>
<td>Li$_2$Se</td>
<td>SeO$_2$</td>
<td>966</td>
<td>483</td>
<td>0.5</td>
</tr>
<tr>
<td>Sr</td>
<td>Li$_{23}$Sr$_6$</td>
<td>SrO</td>
<td>517</td>
<td>992</td>
<td>1.9</td>
</tr>
<tr>
<td>Ru</td>
<td>LiRu$_3$</td>
<td>RuO$_2$</td>
<td>806</td>
<td>67</td>
<td>0.1</td>
</tr>
<tr>
<td>Rh</td>
<td>LiRh</td>
<td>Rh$_2$O$_3$</td>
<td>634</td>
<td>211</td>
<td>0.3</td>
</tr>
<tr>
<td>Pd</td>
<td>Li$_3$Pd</td>
<td>PdO</td>
<td>438</td>
<td>1095</td>
<td>2.5</td>
</tr>
<tr>
<td>Cd</td>
<td>Li$_3$Cd</td>
<td>CdO</td>
<td>418</td>
<td>626</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Figure 1.15. Discharge capacity of melt-spun Al/Si/Mn alloys depending on cycle number.\textsuperscript{59}
Sohn et al.\textsuperscript{56} reported that the cycle performance of nanosized Cu$_6$Sn$_5$ electrode is significantly enhanced in comparison with that of the same material prepared by sintering or mechanical alloying because of nanosized active material and recovery of the Cu$_6$Sn$_5$ intermetallic structure. The cycle performance of Li/Cu$_6$Sn$_5$ and Li/Sn cells in the voltage range 0.0-1.2V is shown in Figure 1.16. Cu$_6$Sn$_5$ alloy has shown a better capacity-retention characteristic than Sn.

![Figure 1.16. Capacity vs. cycle number plots for Li/Cu$_6$Sn$_5$ and Li/Sn cells in the range of 0.0-1.2 V.\textsuperscript{56}](image)

Whittingham et al.\textsuperscript{60} produced manganese-oxide nanofibers by the electrospinning of poly-methyl methacrylate gels containing manganese salts. These nanofibers showed reversible electrochemical activity in lithium cells. The electrospun fibers have average diameters of 100–300 nm, the fibrous morphology remains (Mn$_3$O$_4$) after removal of the
organic polymer and have high specific capacity (more than 450 mAh g$^{-1}$ for at least 50 cycles).

Sohn et al.$^{61}$ prepared alloys of Mg$_{0.5}$Ni$_{0.5}$, Mg$_{0.67}$Ni$_{0.33}$ and Mg$_{0.75}$Ni$_{0.25}$ by mechanical alloying and they reported that Li was alloyed and dealloyed reversibly with Mg at very low voltage region below 100 mV, and the initial capacity obtained was approximately 3070 mAh g$^{-1}$. Mg$_{0.5}$Ni$_{0.5}$ was amorphous and Mg$_{0.67}$Ni$_{0.33}$ was crystalline, while Mg$_{0.75}$Ni$_{0.25}$ was a mixture of Mg and Mg$_2$Ni phases. It was demonstrated that only Mg$_{0.75}$Ni$_{0.25}$ reacted significantly with Li at room temperature while Mg$_{0.67}$Ni$_{0.33}$ reacted with Li at high temperature. Mg$_{0.75}$Ni$_{0.25}$ shows enhanced cycle performance compared to that of pure Mg (Figure 1.17).

![Figure 1.17. Cycle performances of Mg and Mg$_{0.75}$Ni$_{0.25}$ electrodes. ](image)
Figure 1.18. Cycle performances and schematic diagrams of Si/carbon composites/Li cell: (a) discharge capacity; (b) efficiency; (c) MC (microsize) and (d) NC (nanosize).\textsuperscript{62}

Senna \textit{et al.}\textsuperscript{62} reported that the nanometer Si/carbon composite anode electrode shows better cyclability compared to conventional micron-sized Si/carbon composites. As can be seen from Figure 1.18, the combination of composite fabrication with carbon materials in nanosize and the downsizing of Si powder improve the cyclability of Li-ion battery.

1.4.2. Cathode materials for lithium-ion batteries

To date, many types of materials have been investigated as cathode materials for lithium-ion batteries. Commonly used cathode materials for lithium ion batteries are LiCoO\textsubscript{2}, LiNiO\textsubscript{2}, LiMn\textsubscript{2}O\textsubscript{4}, and LiFePO\textsubscript{4}.\textsuperscript{63} Comparison of specific capacity ranges of cathode materials for lithium-ion batteries with different crystal structures is shown in Figure 1.19.
1.4.2.1. Layered lithium-metal oxides

Shukla et al.\textsuperscript{49} reported that lithiated nickel and cobalt oxides, LiMO\textsubscript{2} (M= Ni, Co or Ni/Co) are the most studied cathodes for lithium-ion batteries. Structure of layered LiMO\textsubscript{2} is shown in Figure 1.20a. Layer structured LiCoO\textsubscript{2} is the most widely used material for commercial production, because of its simple preparation. Its average capacity is 140 mAh g\textsuperscript{-1}. In addition to these, LiCoO\textsubscript{2} has various drawbacks including various cost and environmental risks.\textsuperscript{63} LiNiO\textsubscript{2} has same crystal structure with LiCoO\textsubscript{2} and it is shown in Figure 1.20a. Its working voltage is more than 3.7 V and theoretical capacity is 275 mAh g\textsuperscript{-1}. 

Figure 1.19. Comparison of different cathode materials in terms of their crystal structures.
The LiNiO$_2$ provides important advantages, such as less toxicity, lower price and higher reversible capacity (200 mAh g$^{-1}$) as compared to LiCoO$_2$. However, it suffers from a few problems, such as irreversible phase transformation, difficulty in synthesis due to its tendency to form Ni-rich, non-stoichiometric phases, thermal instability and safety concerns.

Wan et al.\textsuperscript{64} reported the initial discharge capacity of layered structure LiNiO$_2$ material, prepared at low temperatures, is 169.5 mAh g$^{-1}$ and the initial coulombic efficiency is 92.4%. As can be seen from Figure 1.21, LiNiO$_2$ cathode exhibits good electrochemical performance.
1.4.2.2. Lithium-manganese spinels

Lithium-manganese oxides with the spinel structure are of interest as lithium insertion electrodes for rechargeable lithium batteries. Structure of the cubic spinel LiMn$_2$O$_4$ (lithium manganese oxide) is shown in Figure 1.20b.$^{49}$ A spinel compound, LiMe$_x$Mn$_{2-x}$O$_4$ (Me = Metal element), is an attractive cathode material for replacing Co or Ni based layered cathode materials in the next generation of Li-ion batteries. Especially, it has been extensively studied as positive electrode materials of large-size lithium-ion batteries for power sources of hybrid electric vehicles, because they have several advantages such as lower cost, high-rate capability and higher thermal stability compared to those of Co or Ni based layered materials. The main obstacle to commercialize LiMn$_2$O$_4$ is the significant capacity fading at elevated temperatures. A slight lithium ions deficiency causes the
tetragonal phase formation provided that the materials obtained at high temperatures are rapidly quenched in the solid CO₂. On the contrary, a small amount of excess lithium can influence the cubic → orthorhombic phase transition observed for stoichiometric LiMn₂O₄.⁶⁵-⁶⁷

Figure 1.22. The structure of (a) cubic spinel and (b) orthorhombic LiMn₂O₄.⁶⁷

1.4.2.3. Olivines

Padhi et al.⁶⁸ first demonstrated that orthorhombic LiFePO₄ could be used as a cathode for rechargeable lithium-ion batteries. It has a theoretical capacity of 170 mAh g⁻¹ and is environmentally benign and cheaper to produce compared with LiCoO₂. Furthermore, it shows excellent cycle stability due to structural similarity between charged/discharged states. Specially, this material exhibits very good thermal stability. These properties make it an attractive candidate for large scale batteries, such as power sources for electric vehicles and
hybrid electrical vehicles. Crystal structures of LiFePO$_4$ and FePO$_4$ are shown in Figure 1.23. Charge/discharge reactions can be written as follows:

\[
\text{LiFePO}_4 - x\text{Li}^+ - xe^- \rightarrow x\text{FePO}_4 + (1 - x)\text{LiFePO}_4 \text{ (charge)} \quad (1.1)
\]

\[
\text{FePO}_4 + x\text{Li}^+ + xe^- \rightarrow x\text{LiFePO}_4 + (1 - x)\text{FePO}_4 \text{ (discharge)} \quad (1.2)
\]

Figure 1.23. Crystal structures of (a) LiFePO$_4$ and (b) a layer of the LiO$_6$ along the b–c plan shows the two lithium diffuse passes along b-axis and c-axis.$^{69}$

Sony’s typical production route for LiMPO$_4$-type cathode composites is given in Figure 1.24.$^{70}$ Crystal structure and production methods of LiFePO$_4$ will be analyzed in detail in the Chapter 1.5.
1.5. Overview of LiFePO$_4$

Among various alternative cathode materials, lithium iron phosphate (LiFePO$_4$), which was discovered by Goodenough in 1997$^{71}$, is gaining significant attention because of its relatively low cost, high discharge potential (very flat voltage curve around 3.4 V versus Li/Li$^+$), large specific capacity (170 mAh g$^{-1}$), good thermal stability, excellent cycling performance, and high abundance with the environmentally benign and safe nature. However, LiFePO$_4$ also has its own limitation such as low conductivity ($\sim$10$^{-9}$ S cm$^{-1}$), which leads to high impedance and low rate capability for batteries using that material.$^{71}$ Approaches to solve that problem include but not limited to: doping LiFePO$_4$ with supervalent cations that enhance the material conductivity at the crystal level,$^{72, 73}$ coating LiFePO$_4$ with conductive materials such as carbons from organic precursors,$^{74, 75}$ and
decreasing the particle size of LiFePO$_4$ in order to make the diffusion path of lithium shorter.$^{76, 77}$ These approaches can be realized by using novel fabrication technologies.

This chapter presents an overview of recent advances in the fabrication of high-performance LiFePO$_4$ powders for lithium-ion batteries. The LiFePO$_4$ powder fabrication methods covered include: solid-state synthesis, mechanochemical activation, carbothermal reduction, microwave heating, hydrothermal synthesis, sol-gel synthesis, spray pyrolysis, coprecipitation, microemulsion drying, and others. The impacts of these fabrication methods on the structure and performance of LiFePO$_4$ powders are discussed. In addition, the improvement of the conductivity of LiFePO$_4$ powders through novel powder technologies is addressed.

1.5.1. Crystal structure of LiFePO$_4$

LiFePO$_4$ has an ordered olivine structure with a Pnma space group, in which P atoms (PO$_4$) reside within tetrahedral 4c sites, and Fe and Li cations (FeO$_6$ and LiO$_6$) reside within octahedral 4c and 4a sites, respectively, as shown in Figure 1.25. Oxygen atoms show slightly distorted hexagonal close packed arrangement.$^{48, 71}$ FeO$_6$ is a corner shared octahedron and PO$_4$ is an edge-shared tetrahedron, and they form the zigzag skeleton by sharing oxygen and Li ions locate in the octahedral channels. The FeO$_6$ octahedra are connected through the corners in the bc plane and LiO$_6$ grows as a linear chain along the b
axis and a PO₄ tetrahedral shares the edges with one FeO₆ and two LiO₆. The PO₄ tetrahedral structure is the reason for the good phase stability during lithium deintercalation.⁴⁸, ⁶⁸, ⁷⁸-⁸¹

Figure 1.25. Crystal structure of LiFePO₄.

LiFePO₄ powders can be prepared by both solid-state and solution-based methods. Solid-state techniques are carried out at high temperatures without any solvent addition. On the other hand, solution-based methods are based on reactions that take place with the presence of appropriate solvent systems.
1.5.2. Solid-state methods for LiFePO$_4$ production

Solid-state synthesis, mechanochemical activation, carbothermal reduction and microwave heating are based on solid-state chemistry and are the most common solid-state methods for preparing LiFePO$_4$ powders. Figure 1.26 shows typical routes used in these solid-state methods. Solid state methods are of importance in terms of obtaining ordered crystal structure in a simple way at elevated temperatures.

* In the microwaving heating method, the calcination step is carried out using microwave energy.

Figure 1.26. Typical routes for producing LiFePO$_4$ powders using solid-state methods.
1.5.2.1. Solid-state synthesis

Solid-state synthesis is a technique used to produce chemical structures by reactions carried out at extreme conditions, such as high temperature and pressure, without any solvent. This method is generally used for the mass production of unique, advanced structures, such as special ceramics, scintillation crystals, and piezoelectrics. LiFePO$_4$ powders can be fabricated using the solid-state synthesis method and Table 1.2 shows typical precursors used in this method and the particle size and discharge capacity of the resultant LiFePO$_4$ powders. The most commonly used precursors are Li$_2$CO$_3$ or LiOH·H$_2$O for Li, FeC$_2$O$_4$·2H$_2$O or Fe(C$_2$O$_4$)$_2$ for Fe, and NH$_4$H$_2$PO$_4$ for PO$_4$, respectively. However, other precursors can also be used. For example, Wang et al.\textsuperscript{87} used LiF to replace LiOH·H$_2$O and Li$_2$CO$_3$ and obtained LiFePO$_4$ powders with an average particle diameter of around 500 nm. These LiFePO$_4$ powders have good electrochemical performance, but the release of HF gas, a byproduct of reaction, should be appropriately managed during powder production.

The solid-state synthesis of LiFePO$_4$ powders typically starts with the mixing of precursors by ball-milling or other techniques (Figure 1.23). For example, Fey et al.\textsuperscript{88} prepared LiFePO$_4$/C powder by ball milling of mixed precursors for 3, 12 and 18 hours, followed by heat treatment at 600°C. An 18 hour ball-milling time was found to produce LiFePO$_4$ powders that have an average particle size of 188 nm and a good discharge capacity of 161 mAh g$^{-1}$ at 0.1 C with good cycling performance. In addition to ball milling,
precursors can also be mixed by generating dispersion in a solvent such as acetone, followed by solvent evaporation.\textsuperscript{82, 86, 89-92}

Mixed precursors can be pelletized and then calcined using one-step heat treatment. For example, Li \textit{et al}.\textsuperscript{93} prepared LiFePO\textsubscript{4} powders by one-step heat treatment under vacuum at 700°C for 10 h. The resultant LiFePO\textsubscript{4} powders have a particle size of 1 µm with a few aggregations, and the discharge capacity is around 111 mAh g\textsuperscript{-1}. Although one-step heat treatment is convenient\textsuperscript{84}, prepared mixtures are more often heat treated in two steps. The first step (precalcination) is carried out at 250 - 350°C, which is designed for the decomposition of the precursors and expelling of the gases. The second step is the final calcination of powders, which occur at relatively high temperatures (400 - 800°C). The calcination temperature has an important effect on the structure, particle size (particle growth), and discharge capacity of LiFePO\textsubscript{4} powders. For example, Yamada \textit{et al}.\textsuperscript{82} synthesized LiFeO\textsubscript{4} powders by solid-state synthesis at different temperatures and found that the highest discharge capacity of 162 mAh g\textsuperscript{-1} was obtained by calcining the homogeneously mixed precursors at 500 - 600°C. Takahashi \textit{et al}.\textsuperscript{94} also fabricated LiFePO\textsubscript{4} powders by solid-state synthesis and found that the optimum calcination temperature for achieving the highest discharge capacity was 675°C. In addition to the calcination temperature, it is also important to control the calcination atmosphere for avoiding oxidized byproducts, such as Fe\textsubscript{2}O\textsubscript{3} and Li\textsubscript{3}Fe\textsubscript{2}(PO\textsubscript{4})\textsubscript{3}.\textsuperscript{82, 89, 91, 92} Atmospheres that can be used include inert (Ar), slightly reductive (Ar-H\textsubscript{2}), reductive (H\textsubscript{2}-N\textsubscript{2} or N\textsubscript{2}), \textsuperscript{70, 82, 89, 91-93, 95, 96} and vacuum conditions.\textsuperscript{93}
Table 1.2. Precursors used in the solid-state synthesis method, and particle size and electrochemical performance of the resultant LiFePO₄ powders.

<table>
<thead>
<tr>
<th>Li Precursor</th>
<th>Fe Precursor</th>
<th>P Precursor</th>
<th>Metal Dopant</th>
<th>Molar Ratio</th>
<th>Carbon Source</th>
<th>Product</th>
<th>Particle Size (nm)</th>
<th>Discharge Capacity (mAh g⁻¹)</th>
<th>Ref</th>
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<td>Li₂CO₃</td>
<td>Fe(CH₃CO₂)₂</td>
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<td></td>
<td></td>
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<td>NH₄H₂PO₄</td>
<td>1:1:1</td>
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<td>84</td>
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<td>NH₄H₂PO₄</td>
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<td>149 (C/5)</td>
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<td>FePO₄·(H₂O)₂</td>
<td>1:1</td>
<td>Cellulose acetate/sucrose</td>
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<td>160 (C/4)</td>
<td></td>
<td></td>
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<td>NH₄H₂PO₄</td>
<td>1.03:1:1</td>
<td>Malonic acid</td>
<td>LiFePO₄/C</td>
<td>188</td>
<td>161 (C/10)</td>
<td></td>
<td>88</td>
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<td>NH₄H₂PO₄</td>
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<td>NH₄H₂PO₄</td>
<td>1:1:1</td>
<td>LiFePO₄</td>
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<td></td>
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<td>NH₄H₂PO₄</td>
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<td>LiFePO₄</td>
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<td>FeC₂O₄·2H₂O</td>
<td>NH₄H₂PO₄</td>
<td>1:1:1</td>
<td>LiFePO₄</td>
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<tr>
<td>LiClO₄</td>
<td>FeC₂O₄·2H₂O</td>
<td>NH₄H₂PO₄</td>
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<td>LiFePO₄</td>
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<td></td>
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<tr>
<td>LiClO₄</td>
<td>FeC₂O₄·2H₂O</td>
<td>NH₄H₂PO₄</td>
<td>1:1:1</td>
<td>LiFePO₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>105</td>
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</tbody>
</table>

Note: Refer to the corresponding literature for detailed information and conditions of synthesis. The discharge capacity values are for C/10, C/5, or C/100 rates, where applicable.
One limitation of pure LiFePO$_4$ powders is their low electrical conductivity, which results in poor rate capability. In solid-state synthesis, the conductivity of LiFePO$_4$ powders can be improved by introducing conductive carbon, which can be obtained by directly adding a carbon source into the precursors. Yun et al.$^{84}$ prepared LiFePO$_4$/C powders by solid-state synthesis using polyvinyl alcohol (PVA) as a carbon source. The presence of PVA prevents the particle growth during calcination because the polymer decomposes around the same temperature of LiFePO$_4$ formation. As a result, these LiFePO$_4$/C powders have small particle sizes ranging from 200 to 300 nm. The achieved maximum capacity in that work was 156 mAh g$^{-1}$, but the cycling performance was poor.

The performance of LiFePO$_4$/C powders can be improved by using other carbon sources to replace PVA. Fey et al.$^{85}$ used malonic acid as a carbon source, and the resultant LiFePO$_4$/C powders (100 – 200 nm) have a discharge capacity 149 mAh g$^{-1}$ at 0.2 C and a good cycling performance. In addition to malonic acid, other carbon sources that have been studied include but not limited to chitosan, glucose, cellulose acetate, and sucrose.$^{86,101,102}$

In addition to carbon, metal dopants can be added in solid-state synthesis to adjust the structure and performance of LiFePO$_4$ powders. Mi et al.$^{103}$ used Nb$_2$O$_5$ as a metal dopant to form Nb-doped Li$_{0.99}$Nb$_{0.01}$FePO$_4$ powders by solid state synthesis. MnCO$_3$ has also been used as a metal dopant to produce LiFe$_y$Mn$_{1-y}$PO$_4$ powders with enhanced conductivity.
Solid-state synthesis is of importance in terms of obtaining unique structures; however, reactions take place in a solid phase, which requires high temperature, high energy, long processing time, repeated grinding, and special atmosphere. As a result, the product cost of solid-state synthesis is relatively high.

1.5.2.2. Mechanochemical activation

Mechanochemical activation is one of the most common methods for preparing metal and alloy powders, and is mainly based on increasing the chemical reactivity of the mixtures by high-energy ball milling. The main reasons for the enhancement of reactivity can be given as: the formation of free valences on the outermost layer of the material and the increase in the surface area where reactions take place. Mechanochemical activation enables the preparation of powders with relatively low particle size and high surface area. However, mechanochemical activation also has some drawbacks, such as higher impurity stemmed from the milling medium and the rise of temperature during the high-energy milling process.\(^{105}\) For the synthesis of LiFePO\(_4\) powders, the temperature rise during high-energy ball milling may contribute to the decomposition of precursors, but is not sufficient for the formation of LiFePO\(_4\) crystalline structure.\(^{105-107}\) Therefore, mechanochemical activation is generally used as a preparation step prior to the classical solid-state synthesis, and the aim is to have the smallest possible particle size to drive the reactions at lower temperatures.
Franger et al.\textsuperscript{79} compared different synthesis methods and found that LiFePO$_4$ powders prepared by the mechanochemical activation have pure, uniform, and well-crystallized structure, and present higher specific capacity (150 mAh g$^{-1}$ at 0.2 C) than those prepared by conventional solid-state synthesis.

Table 1.3 shows typical precursors used in the mechanochemical activation method and the particle size and electrochemical performance of the resultant LiFePO$_4$ powders. As shown in Figure 1.26, typical procedure starts with activating mixed precursors using high-energy ball-milling for 3 - 15 hours, depending on the desired particle size, in air\textsuperscript{108} or in an inert atmosphere.\textsuperscript{109} Mechanochemically activated mixtures are then pelletized and calcined at elevated temperatures at 600 - 900°C in appropriate atmosphere such as 95% Ar + 5% H$_2$,\textsuperscript{108} N$_2$,\textsuperscript{42, 109, 110} or vacuum\textsuperscript{111} for 0.5 - 10 hours.\textsuperscript{108, 109, 111}

To improve the electrical conductivity of LiFePO$_4$ powders, carbon materials, such as graphite, carbon black, and acetylene black, can be added to the mixtures during high-energy ball milling.\textsuperscript{108} As reported by Shin \textit{et al.},\textsuperscript{108} among these three carbon materials, graphite gave the highest conductivity with the highest stability and capacity (141 mAh g$^{-1}$ at 0.1 C) because of its low charge transfer resistance and low ion migration resistance. The dispersion of carbon in LiFePO$_4$/C composite powders is important. Porcher \textit{et al.}\textsuperscript{112} investigated the effect of surfactants on the dispersion of carbon black in the LiFePO$_4$/C powders, which were produced by using mechanochemical activation. In their work, three different types of surfactants (anionic, non-ionic, and cationic) were added during the electrode preparation
process. It was found that non-ionic surfactant (Triton X-100) led to more homogeneous carbon dispersion and the resultant LiFePO$_4$/C powders have better electrochemical performance than those prepared using ionic surfactants.

In addition to carbon, Fe$_2$P can be used to modify the conductivity of LiFePO$_4$ powders. Kim et al.$^{111}$ produced pure LiFePO$_4$ and LiFePO$_4$/Fe$_2$P powders by mechanochemical activation, followed by calcination at 900°C for different time intervals under $10^{-6}$ Torr pressure. Pure LiFePO$_4$ showed a discharge capacity of 162 mAh g$^{-1}$ and good capacity retention. As reported, Fe$_2$P had an important effect on the conductivity of the powders, especially at higher concentrations; however, lower capacity values were obtained mainly because of the increase in particle size and decrease in surface area. Maximum initial discharge capacity obtained was 113 mAh g$^{-1}$ for LiFePO$_4$/Fe$_2$P powders (Fe$_2$P: 8 wt%).

The particle sizes of LiFePO$_4$ and LiFePO$_4$/C powders prepared by mechanochemical activation are typically in the range of 60 - 300 nm.$^{108,109}$ In addition to conventional mechanochemical activation, modified methods can be designed to further reduce the particle size. Kim et al.$^{109}$ prepared LiFePO$_4$/C powders by mixing the precursors with distilled water for 7 hours, evaporating the water, high-energy ball milling for 15 h under Ar atmosphere, powder pressing in order to obtain pellets, and thermal processing at 600°C for 10 h under N$_2$ atmosphere. Using this modified mechanochemical activation method, the particle size of the resultant LiFePO$_4$/C powders reduced from 60 - 115 nm to 65 - 90 nm. As a result, the modified method gave better and more uniform carbon coating, larger specific surface area,
and higher electronic conductivity. The discharge capacity for LiFePO$_4$/C powders obtained by the modified method is 166 mAh g$^{-1}$ at 0.1 C and 154 mAh g$^{-1}$ at 0.5 C, respectively.
Table 1.3. Precursors used in the mechanochemical activation method, and particle size and electrochemical performance of the resultant LiFePO₄ powders.

<table>
<thead>
<tr>
<th>Li Precursor</th>
<th>Fe Precursor</th>
<th>P Precursor</th>
<th>Carbon Source</th>
<th>Molar Ratio</th>
<th>Product</th>
<th>Particle Size (nm)</th>
<th>Discharge Capacity (mAh g⁻¹)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₃PO₄</td>
<td>Fe₃(PO₄)₂·5H₂O</td>
<td>Sucrose</td>
<td>1:1</td>
<td>LiFePO₄/C</td>
<td>150 (C/5)</td>
<td>97</td>
<td></td>
<td></td>
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<tr>
<td>Li₂CO₃</td>
<td>FeC₅O₄·2H₂O</td>
<td>(NH₄)₂HPO₄</td>
<td>Graphite</td>
<td>1:1:1</td>
<td>LiFePO₄/C</td>
<td>100-300</td>
<td>141 (C/10)</td>
<td>108</td>
</tr>
<tr>
<td>Li₂CO₃</td>
<td>FeC₅O₄·2H₂O</td>
<td>(NH₄)₂HPO₄</td>
<td>Acetylene black</td>
<td>1:1:1</td>
<td>LiFePO₄/C</td>
<td>60-115</td>
<td>152 (C/10)</td>
<td>109</td>
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<tr>
<td>Li₂CO₃</td>
<td>FeC₅O₄·2H₂O</td>
<td>(NH₄)₂HPO₄</td>
<td>Acetylene black</td>
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<td>LiFePO₄/C</td>
<td>65-90</td>
<td>166 (C/10)</td>
<td>109</td>
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</table>
1.5.2.3. Carbothermal reduction

In both conventional solid-state synthesis and mechanochemical activation methods, Fe(II) compounds are used as the Fe precursor for LiFePO$_4$ powders. However, it is often challenging to prevent the oxidation of unstable Fe(II), which tends to form Fe(III) as the impurity during the LiFePO$_4$ formation. Recently, carbothermal reduction is gaining attention because it allows the direct use of Fe(III) compounds as Fe precursor. In general, Fe(III) compounds are relatively cheap, readily available, and chemically stable when compared with Fe(II) compounds.$^{118-120}$

Carbothermal reduction is a high-temperature reduction reaction, which utilizes a carbon source as the reducing agent. Carbon black, graphite, and pyrolyzed organic chemicals are commonly used reducing agents. Carbothermal reduction is a highly endothermic reaction, and hence the critical energy, which is given to the synthesis environment, must be high enough to drive the reaction. In addition, since solid carbon is used as the reducing agent, it is important to keep all precursors/reactants in good contact with each other throughout the reaction. The mechanism and reaction rate are closely related with the particle sizes of precursors and reducing agents, mixing conditions, diffusion rates, gas concentration, and impurities in the environment.$^{118, 121, 122}$ Properties of the resultant powders depend on the processing conditions such as temperature, pressure, precursors, and reducing agents.
When used to produce LiFePO₄ powders, the carbothermal reduction method is excellent for the reduction of Fe(III), stabilization of Fe(II), control of particle morphology, and enhancement of electrical conductivity by coating LiFePO₄ with residual carbon. Studies show that, compared with other solid-state methods, carbothermal reduction is an energy efficient approach to produce LiFePO₄ powders with fine, uniform particle morphology and high capacity.⁴⁸, ¹¹⁸, ¹¹⁹, ¹²³ Table 1.4 shows the precursors used in the carbothermal reduction method, and the particle size and discharge capacity of the resultant LiFePO₄ powders. Typical procedure includes two major steps: mixing stoichiometric amounts of precursors and reducing agents by ball milling for 2 – 4 hours, and calcining (generally without precalcination) the mixtures at a temperature between 550 and 850°C for 8 - 10 hours in an inert atmosphere, such as N₂ or Ar (Figure 1.26). During the calcination process, two main carbon oxidation reactions occur to reduce Fe(III) to Fe(II)¹¹⁸:

\[
C + O₂ \rightarrow CO₂ \quad (T < 650°C) \quad \text{(1.3)}
\]

\[
2C + O₂ \rightarrow 2CO \quad (T > 650°C) \quad \text{(1.4)}
\]

Both the volume and entropy changes in Reaction (1.3) are negligible and the reaction produces less reductive atmosphere. However, Reaction (1.4) occurs at temperatures higher than 650°C, which results in a stronger reducing condition than Reaction (1.3), and the volume and entropy increases are significant.¹¹⁸
In carbothermal reduction, processing conditions, especially calcination temperature, are of great importance for the morphological and electrochemical performance of the resultant powders. Mi et al.\textsuperscript{123} synthesized LiFePO\textsubscript{4}/C powders by using FePO\textsubscript{4} as the Fe precursor and polypropylene as the reducing agent and carbon source. Calcination was carried out at 650°C for 10 h under N\textsubscript{2} atmosphere without any pre-calcination step. The pyrolysis of polypropylene during the calcination ensured the reduction of Fe(III) to Fe(II). The resultant LiFePO\textsubscript{4}/C powders have homogeneous carbon coating with particle sizes ranging from 100 to 300 nm. Initial discharge capacity was 160 mAh g\textsuperscript{-1} (0.1 C) at 30 °C. Liu et al.\textsuperscript{124} synthesized LiFePO\textsubscript{4}/C powders by the carbothermal reduction method using different calcination temperatures. The best calcination temperature was reported as 750°C, which produced powders with an initial discharge capacity of 133 mAh g\textsuperscript{-1} at 0.1 C and capacity retention of 96% after 20 cycles. Liu et al.\textsuperscript{125} used cheap Fe\textsubscript{2}O\textsubscript{3} as the Fe source and carbon black and glucose as the reducing agent and carbon source. The effects of calcination temperature on the particle size and electrochemical performance of LiFePO\textsubscript{4}/C powders were investigated. When the precursors were treated with glucose at 700°C for 8 h, the best performance was obtained: the capacity was 159 mAh g\textsuperscript{-1} at 0.1 C and the cycling fading was 2.2% at the end of 30 cycles. It was also found that the use of high concentration carbon source not only decreased the particle size but also enhanced the cycle life.

The distribution of particle size can also be controlled during the carbothermal reduction. Wang et al.\textsuperscript{126} synthesized LiFePO\textsubscript{4}/C powders by using FePO\textsubscript{4} as the iron source and
glucose as the reducing agent and carbon source. LiFePO$_4$/C powders with uniform particle size distribution were obtained when the precursors were calcined at 650°C for 9 h. The discharge capacities of these powders are 151 mAh g$^{-1}$ at 0.2 C rate and 144 mAh g$^{-1}$ at 1 C rate, respectively. Zhong et al.$^{127}$ prepared high tab-density LiFePO$_4$/C powders by the carbothermal reduction method using Fe$_2$O$_3$ and ferric citrate as the Fe iron source with an equimolar ratio. It was found that the resultant LiFePO$_4$/C powders consisted of nanometer-sized and micrometer-sized particles, and showed trimodal particle size distribution with good discharge capacity (135 mAh g$^{-1}$ at 0.1 C). In these powders, the small particles filled the free space between the bigger particles, and led to high tap density (1.4 g cm$^{-3}$).

In addition to particle size and its distribution, the processing conditions also influence the crystallization degree of LiFePO$_4$ powders. One important contribution of high crystallization degree is that it can suppress the dissolution of LiFePO$_4$ during cycling and leads to improved cycling behavior.$^{128}$ Therefore, in order to obtain good electrochemical performance, it is important to determine the optimum crystallization degree. Zhi et al.$^{128}$ studied the effect of calcination temperature on the crystallinity degree and electrochemical performance of LiFePO$_4$/C powders obtained by carbothermal reduction. It was found that the powders calcined at lower temperatures have lower degree of crystallization with nanosized structure, which leads to higher electrochemical activity and larger initial discharge capacity. But, they showed unsatisfactory cycling performance because of their metastable structures.
To obtain optimized powder structure and performance, modified carbothermal reduction methods were also developed. Liu et al.\textsuperscript{129} designed a modified process by introducing amorphous gel precursor into conventional carbothermal reduction, and they obtained LiFePO$_4$/(C+Fe$_2$P) and LiFePO$_4$/C composite powders. While LiFePO$_4$/C showed a discharge capacity of 146 mAh g$^{-1}$, LiFePO$_4$/(C+Fe$_2$P) has a higher capacity of 157 mAh g$^{-1}$, which was attributed to the enhanced conductivity caused by Fe$_2$P in the structure. Yu et al.\textsuperscript{130} prepared LiFePO$_4$/C powders by combining carbothermal reduction with spray drying and used different carbon sources (such as carbon black, sucrose, citric acid and polyethylene glycol (PEG)) as the reducing agents. As reported, the best electrochemical performance was obtained from citric acid-added powders, which were calcined at 539 °C. It was also found that 453°C was the crystallization temperature of LiFePO$_4$, 539 °C was the transform temperature from Li$_3$Fe$_2$(PO$_4$)$_3$ to LiFePO$_4$, 840 °C was the formation temperature of LiFePO$_4$/C with an excess of Fe$_2$P impurity phase, and 938 °C was the decomposition temperature of LiFePO$_4$/C. Recently, Zhu et al.\textsuperscript{119} synthesized LiFePO$_4$ powders from FeSO$_4$·7H$_2$O and NH$_4$H$_2$PO$_4$ by combining the carbothermal reduction and aqueous precipitation methods. The resultant LiFePO$_4$/C powders showed capacities ranging from 95 - 156 mAh g$^{-1}$ at 0.1 C, depending on the processing conditions.
Table 1.4. Precursors used in the carbothermal reduction method, and particle size and electrochemical performance of the resultant LiFePO$_4$ powders.

<table>
<thead>
<tr>
<th>Li Precursor</th>
<th>Fe Precursor</th>
<th>P Precursor</th>
<th>Metal Dopant</th>
<th>Reducing Agent and Carbon Source</th>
<th>Molar Ratio</th>
<th>Product</th>
<th>Particle Size (nm)</th>
<th>Discharge Capacity (mAh g$^{-1}$)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiH$_2$PO$_4$</td>
<td>Fe$_2$O$_3$</td>
<td></td>
<td>Mg(OH)$_2$</td>
<td>Carbon</td>
<td>1:0.45:0.1</td>
<td>LiFe$<em>{0.9}$Mg$</em>{0.1}$PO$_4$</td>
<td>100,000</td>
<td>151 (C/20)</td>
<td>118</td>
</tr>
<tr>
<td>Li$_2$CO$_3$</td>
<td>FeSO$_4$·7H$_2$O</td>
<td>NH$_4$H$_2$PO$_4$</td>
<td></td>
<td>Carbon</td>
<td>1:2:2</td>
<td>LiFePO$_4$/C</td>
<td>100-300</td>
<td>156 (C/10)</td>
<td>119</td>
</tr>
<tr>
<td>Li$_2$CO$_3$</td>
<td>FePO$_4$·4H$_2$O</td>
<td></td>
<td></td>
<td>Acetylene black</td>
<td>1:2</td>
<td>LiFePO$_4$/C</td>
<td>1,000-3,000</td>
<td>133 (C/10)</td>
<td>124</td>
</tr>
<tr>
<td>Li$_2$CO$_3$</td>
<td>Fe$_2$O$_3$</td>
<td>NH$_4$H$_2$PO$_4$</td>
<td></td>
<td>Glucose, Carbon black</td>
<td>1:1:1</td>
<td>LiFePO$_4$/C</td>
<td>300-1,000</td>
<td>159 (C/10)</td>
<td>125</td>
</tr>
<tr>
<td>Li$_2$CO$_3$</td>
<td>FePO$_4$</td>
<td></td>
<td></td>
<td>Glucose</td>
<td>0.5:1</td>
<td>LiFePO$_4$/C</td>
<td>2,490</td>
<td>151 (C/5)</td>
<td>126</td>
</tr>
<tr>
<td>Li$_2$CO$_3$</td>
<td>Fe$_2$O$_3$</td>
<td>(NH$_4$)$_2$HPO$_4$</td>
<td></td>
<td>Ferrocitrate</td>
<td>1:1:1</td>
<td>LiFePO$_4$/C</td>
<td>135 (C/10)</td>
<td></td>
<td>127</td>
</tr>
<tr>
<td>LiH$_2$PO$_4$</td>
<td>Fe$_2$O$_3$</td>
<td></td>
<td></td>
<td>Glucose</td>
<td>2:1</td>
<td>LiFePO$_4$/C</td>
<td>1,330</td>
<td>154 (C/5)</td>
<td>128</td>
</tr>
<tr>
<td>LiOH·H$_2$O</td>
<td>Fe(NO$_3$)$_3$</td>
<td>NH$_4$H$_2$PO$_4$</td>
<td></td>
<td>C$_2$H$_8$O$_2$:H$_2$O, Sucrose</td>
<td>1:1:1</td>
<td>LiFePO$_4$/C+(Fe$_2$P)</td>
<td>36</td>
<td>157 (C/10)</td>
<td>129</td>
</tr>
<tr>
<td>Li$_2$CO$_3$</td>
<td>Fe(NO$_3$)$_3$·9H$_2$O</td>
<td>NH$_4$H$_2$PO$_4$</td>
<td></td>
<td>Citric acid</td>
<td>1:1:1</td>
<td>LiFePO$_4$/C</td>
<td>150 (C/10)</td>
<td></td>
<td>130</td>
</tr>
<tr>
<td>LiH$_2$PO$_4$</td>
<td>Fe(NO$_3$)$_3$·9H$_2$O</td>
<td></td>
<td></td>
<td>Polycarboxylic acid, Polyhydric alcohol</td>
<td>1:1</td>
<td>LiFePO$_4$/C</td>
<td>134 (C/100)</td>
<td></td>
<td>131</td>
</tr>
</tbody>
</table>
1.5.2.4. Microwave heating

Microwave heating is another easy and useful method for producing LiFePO$_4$ powders.$^{132-136}$ Unlike other solid-state methods, microwave heating is a molecular level heating process, which allows volumetric heating of the material by the absorption of microwave energy. In microwave heating, the heat is generated directly inside the material and is caused by the change of polarization that is activated by the motion of electric charges. Heating rate is controlled by the power of the microwave and heat dissipation occurs through the surface of the material.

Major advantages of microwave heating include good controllability, uniform and selective heating, short processing time (2 - 20 min), reduced energy consumption, and low cost. In addition, microwave heating is a low temperature process with good repeatability and no reductive gas is required for the synthesis of LiFePO$_4$ powders.$^{132-139}$ Higuschi et al.$^{132}$ used the microwave heating method to obtain LiFePO$_4$ powders with an initial discharge capacity of around 125 mAh g$^{-1}$ at 60 °C with low capacity loss. Guo et al.$^{140}$ compared LiFePO$_4$ powders synthesized by microwave heating and solid-state synthesis methods. It was found that microwave-processed LiFePO$_4$ powders have smaller particle size, more uniform size distribution, smoother surface morphology, and higher discharge capacity.
In microwaving processing, a microwave absorber is often added to ensure effective heat generation (Figure 1.26). Table 1.5 shows typical precursors, microwave absorbers, and processing time used in the microwave heating methods. Carbon is the most used microwave absorber because it is low cost, produces rapid heating, and is capable of forming reductive atmosphere, which protects Fe(II) and prevents Fe(III) based impurities. As a result, when carbon is used as the microwave absorber, the formation of LiFePO₄ powders can be directly carried out in air, which significantly lowers the production cost. In addition, the use of carbon can help to reduce the particle size and improves the electrical conductivity of LiFePO₄ powders. Wang et al. used active carbon as a microwave absorber to synthesize nano-sized LiFePO₄ powders, which have a particle size of 40 – 50 nm and discharge capacity of around 112 mAh g⁻¹ at 0.5 C. Although carbon is the most used microwave absorber, other materials can be used to enhance the heat generation efficiency, such as Fe, glucose, and yeast cells.

The microwave heating time is of importance for controlling the particle size and electrochemical performance of the powders. Typically, longer microwave heating time causes larger particle size, lower Li diffusion coefficient, and consequently more capacity loss. In addition to increased particle size, some impurities such as Fe₂P can be observed with prolonged heating time. It was found that the amount of Fe₂P in LiFePO₄ powders is directly proportional to the heating time, and above a critical amount of Fe₂P, LiFePO₄ tends to change into an insulating phase, Li₄P₂O₇. However, when the heating time is too short,
incomplete crystalline structure can form contaminates in the resultant LiFePO₄ powders, which in turn decreases the charge and discharge capacities. Park et al. synthesized LiFePO₄ using the microwave heating method, and found that a heating time of 4 min is sufficient and can produce LiFePO₄ powders that have a specific capacity of 151 mAh g⁻¹ at 0.1 C with stable cycling behavior.

Like most other methods, LiFePO₄ powders produced by microwave heating typically have spherical shape. However, other unique particle structure can be obtained using the microwave heating method. For example, Muraliganth et al. synthesized LiFePO₄ nanorods (width: 25 - 40 nm; length: 0.1 - 1 µm) using microwave heating. These nanorods were mixed with multi-walled carbon nanotubes (MWCNTs) to improve the conductivity, which resulted in a high discharge capacity of around 161 mAh g⁻¹ at 0.1 C with good cyclic performance. Zhou et al. synthesized mesoporous LiFePO₄ powders by using yeast cells as a template for the porous structure. During the formation of LiFePO₄, yeast cells not only connected metal ions chemically but also acted as a reducing agent because of their microwave absorbency. These mesoporous LiFePO₄/C powders have specific capacity of 147 mAh g⁻¹ at 0.1 C and good cycle performance. Jegal et al. also synthesized mesoporous LiFePO₄ spheres, which consisted of smaller particles with average thickness of 2 - 30 nm. The mesoporous structure gave short lithium diffusion length during charge/discharge.

In most cases, traditional continuous microwaves are used to produce LiFePO₄ powders. However, other microwave patterns can also be used. For example, Zou et al. used
intermittent microwave and obtained LiFePO$_4$/C powders with small particle size, ranging from 50 to 100 nm. The powders have enhanced conductivity and improved capacity (162 mAh g$^{-1}$ at 0.1 C).

Microwave heating can also be combined with other methods to produce LiFePO$_4$ powders with controlled structure and performance. Methods that have been combined with microwave heating include: solid-state synthesis,$^{132, 139}$ mechanochemical activation,$^{141, 142}$ sol-gel synthesis,$^{139, 147}$ hydrothermal synthesis,$^{146}$ solvothermal,$^{144}$ and co-precipitation.$^{138, 145}$ For example, Song et al.$^{141}$ combined microwave heating (2 - 5 min) with mechanochemical activation (30 min) to obtain LiFePO$_4$/C powders. The mechanochemical activation decreased the process temperature and led to a uniform distribution of carbon. The average particle size of the resultant LiFePO$_4$/C powders was ≤ 0.64 µm and the discharge capacity was 161 mAh g$^{-1}$ at 0.1 C with a stable capacity retention. Li et al.$^{148}$ synthesized LiFePO$_4$/C powders by combining microwave heating with the co-precipitation method. During the synthesis, beer yeast, a nontoxic, environmentally-friendly, and low cost biosurfactant, was used as a carbon source to increase the material conductivity. Li et al.$^{138}$ also reported the synthesis of LiFePO$_4$ powders by incorporating the solid state synthesis and microwave heating methods, and these powders have a high specific capacity of around 156 mAh g$^{-1}$ at 0.05 C. Zhang et al.$^{139}$ synthesized LiFePO$_4$/C powders by the combination of sol-gel synthesis and microwave heating, and achieved initial specific capacity of 147 mAh g$^{-1}$ at 0.1 C and good cycling performance.
Table 1.5. Precursors, microwave absorbers, power, and time used in the microwave heating method, and particle size and electrochemical performance of the resultant LiFePO$_4$ powders.

<table>
<thead>
<tr>
<th>Li Precursor</th>
<th>Fe Precursor</th>
<th>P Precursor</th>
<th>Microwave Absorber</th>
<th>Power (W)</th>
<th>Time (min)</th>
<th>Carbon Source</th>
<th>Molar Ratio</th>
<th>Product</th>
<th>Particle Size (nm)</th>
<th>Discharge Capacity (mAh g$^{-1}$)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$CO$_3$</td>
<td>Fe(CH$_2$COO)$_2$</td>
<td>NH$_3$HPO$_4$</td>
<td>500</td>
<td>5-20</td>
<td>1:1:1</td>
<td>LiFePO$_4$</td>
<td></td>
<td>95 (C/11)</td>
<td></td>
<td></td>
<td>132</td>
</tr>
<tr>
<td>Li$_2$CO$_3$</td>
<td>Fe(CH$_2$CHOHCOO)$_2$·2H$_2$O</td>
<td>NH$_3$HPO$_4$</td>
<td>Iron Powder</td>
<td>500</td>
<td>5-20</td>
<td>LiFePO$_4$</td>
<td></td>
<td>100 (C/11)</td>
<td></td>
<td></td>
<td>132</td>
</tr>
<tr>
<td>LiOH</td>
<td>(NH$_4$)$_2$Fe(SO$_4$)$_2$·6H$_2$O</td>
<td>H$_3$PO$_4$</td>
<td>Activated Carbon</td>
<td>650</td>
<td>4</td>
<td>Carbon black</td>
<td>1:1:1</td>
<td>LiFePO$_4$</td>
<td>1,000</td>
<td>151 (C/10)</td>
<td>133</td>
</tr>
<tr>
<td>CH$_3$COOLi</td>
<td>FeC$_6$H$_5$PO$_4$·2H$_2$O</td>
<td>NH$_3$HPO$_4$</td>
<td>Activated Carbon</td>
<td>850</td>
<td>A few</td>
<td>Citric acid</td>
<td>1:1:1</td>
<td>LiFePO$_4$</td>
<td>40-50</td>
<td>112 (C/2)</td>
<td>134</td>
</tr>
<tr>
<td>Li$_3$PO$_4$</td>
<td>FeSO$_4$·7H$_2$O</td>
<td>H$_3$PO$_4$</td>
<td>Carbon</td>
<td>300</td>
<td>A few</td>
<td>Glucose</td>
<td>1:1:1</td>
<td>LiFePO$_4$/C</td>
<td>100</td>
<td>117 (C/10)</td>
<td>135</td>
</tr>
<tr>
<td>LiOH</td>
<td>Fe(CH$_2$COO)$_2$</td>
<td>H$_3$PO$_4$</td>
<td>600</td>
<td>5</td>
<td>Poly(3,4-</td>
<td>Ethylenedioxothiophene)</td>
<td>1:1:1</td>
<td>LiFePO$_4$/C</td>
<td>40 ± 6</td>
<td>135 (C/15)</td>
<td>135</td>
</tr>
<tr>
<td>LiOH</td>
<td>Fe(CH$_2$COO)$_2$</td>
<td>H$_3$PO$_4$</td>
<td>600</td>
<td>5</td>
<td>Poly(3,4-</td>
<td>Ethylenedioxothiophene)</td>
<td>1:1:1</td>
<td>LiFePO$_4$/C</td>
<td>40 ± 6</td>
<td>135 (C/15)</td>
<td>135</td>
</tr>
<tr>
<td>CH$_3$COOLi</td>
<td>FeSO$_4$·7H$_2$O</td>
<td>H$_3$PO$_4$</td>
<td>Carbon Black</td>
<td>400</td>
<td>18</td>
<td>Polyethylene glycol</td>
<td>1:1:1</td>
<td>LiFePO$_4$/C</td>
<td>132 - 465</td>
<td>147 (C/10)</td>
<td>139</td>
</tr>
<tr>
<td>LiOH·H$_2$O</td>
<td>FePO$_4$·4H$_2$O</td>
<td>Graphite</td>
<td>700</td>
<td>4</td>
<td>Glucose</td>
<td>1:1:1</td>
<td>LiFePO$_4$/C</td>
<td>160-600</td>
<td>150 (C/10)</td>
<td>139</td>
<td></td>
</tr>
<tr>
<td>Li$_3$PO$_4$</td>
<td>Fe(SO$_3$)$_2$·8H$_2$O</td>
<td>H$_3$PO$_4$</td>
<td>Activated Carbon</td>
<td>750</td>
<td>2.5</td>
<td>Acetylene black</td>
<td>1:1:1</td>
<td>LiFePO$_4$/C</td>
<td>≤640</td>
<td>161 (C/10)</td>
<td>139</td>
</tr>
<tr>
<td>Li$_3$CO$_3$</td>
<td>FePO$_4$·4H$_2$O</td>
<td>H$_3$PO$_4$</td>
<td>1000</td>
<td>3.33</td>
<td>Glucose</td>
<td>1:1:1</td>
<td>LiFePO$_4$/C</td>
<td>50 - 100</td>
<td>162 (C/10)</td>
<td>139</td>
<td></td>
</tr>
<tr>
<td>Li$_3$PO$_4$</td>
<td>Fe(SO$_3$)$_2$·8H$_2$O</td>
<td>H$_3$PO$_4$</td>
<td>750</td>
<td>2</td>
<td>Acetylene black</td>
<td>1:1:1</td>
<td>LiFePO$_4$/C</td>
<td>165 (C/50)</td>
<td></td>
<td>139</td>
<td></td>
</tr>
<tr>
<td>LiOH</td>
<td>Fe(CH$_2$COO)$_2$</td>
<td>H$_3$PO$_4$</td>
<td>600</td>
<td>5</td>
<td>MWCNT</td>
<td>1:1:1</td>
<td>LiFePO$_4$/MWCNT</td>
<td>40 ± 6</td>
<td>161 (C/10)</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>LiOH</td>
<td>Fe(CH$_2$COO)$_2$</td>
<td>H$_3$PO$_4$</td>
<td>600</td>
<td>5</td>
<td>MWCNT</td>
<td>1:1:1</td>
<td>LiFePO$_4$/MWCNT</td>
<td>40 ± 6</td>
<td>161 (C/10)</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>Li$_3$PO$_4$</td>
<td>C$_6$H$_7$FeO$_7$</td>
<td>H$_3$PO$_4$</td>
<td>300</td>
<td>5</td>
<td>MWCNT</td>
<td>1:1:1</td>
<td>LiFePO$_4$/MWCNT</td>
<td>40 ± 6</td>
<td>161 (C/10)</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>CH$_3$COOLi</td>
<td>FeSO$_4$·7H$_2$O</td>
<td>Na$_2$HPO$_4$</td>
<td>Activated carbon, Yeast cells</td>
<td>650</td>
<td>A few</td>
<td>Yeast cells</td>
<td>1:1:1</td>
<td>LiFePO$_4$/C</td>
<td>35-100</td>
<td>147 (C/10)</td>
<td>140</td>
</tr>
<tr>
<td>Li$_2$CO$_3$</td>
<td>FeSO$_4$·7H$_2$O</td>
<td>(NH$_4$)$_2$HPO$_4$</td>
<td>Carbon Black</td>
<td>300</td>
<td>10</td>
<td>Carbon black, Beer yeast</td>
<td>0.3:1:1</td>
<td>LiFePO$_4$/C</td>
<td></td>
<td>140</td>
<td></td>
</tr>
</tbody>
</table>
1.5.3. Solution-based methods for LiFePO₄ production

Although solid-state methods are simple to use, they are typically time and energy consuming techniques and often lead to large particle size, low purity, and relatively poor electrochemical performance. Therefore, solution-based methods are of increasing importance since they often result in smaller and more uniform particle size, higher purity, more homogeneous carbon coating, and higher electrochemical capacity. Hydrothermal synthesis, sol-gel synthesis, spray pyrolysis, co-precipitation, and microemulsion drying are common solution-based methods used for the preparation of LiFePO₄ powders. General production routes are shown schematically in Figure 1.27.

* In the hydrothermal synthesis method, it is possible to avoid the calcination step if no carbon coating is desired.

Figure 1.27. Typical routes for producing LiFePO₄ powders using solution-based methods.
1.5.3.1. Hydrothermal synthesis

Hydrothermal synthesis is a chemical process that occurs in an aqueous solution of mixed precursors above the boiling temperature of water. In hydrothermal synthesis, it is possible to avoid the calcinations step and obtain pure LiFePO₄ powders directly from the heated solution. However, if the carbon coating is desired, it is necessary to carry out the calcination step at higher temperatures. During hydrothermal synthesis, heated water accelerates the diffusion of particles and the crystal growth is relatively fast. Hydrothermal synthesis is typically carried out in a closed system called autoclave and there are less environmental concerns than many other powder production technologies. Therefore, hydrothermal synthesis is a simple, clean, and relatively low-cost method that can be used to produce powders with high uniformity and purity.\(^{149-151}\) Currently, hydrothermal synthesis has been widely used for the synthesis of oxides, silicates, and some specific compounds with unique characteristics.

Hydrothermal synthesis was first used by Yang et al.\(^{152,153}\) to prepare LiFePO₄ powders. As shown in Figure 1.27, standard hydrothermal synthesis starts with the mixing of precursors with the exact stoichiometric ratio in an aqueous solution. After the homogeneous mixing of the precursors, the solution is treated in an autoclave at a temperature above 100°C, generally between 120 – 220 °C for 5 - 10 h. LiFePO₄ powders can then be obtained by drying the slurries or participates.\(^{73,152-158}\) LiFePO₄ powders produced by hydrothermal synthesis are typically low cost, high purity, and have small grain size and large surface area.
In addition, the presence of high-temperature water hinders the oxidation of Fe$^{+2}$ to Fe$^{+3}$. Table 1.6 shows precursors that have been used in the hydrothermal synthesis of LiFePO$_4$ powders.

Like many other methods, carbon sources can be added to the hydrothermally obtained LiFePO$_4$ powders to enhance the conductivity. However, in this case, an additional heat-treatment (or calcination) step should be carried out at elevated temperatures such as 400 – 750 °C for 0.5 - 12 h under N$_2$ or argon atmosphere in order to carbonize the carbon source.$^{152, 156, 159-161}$ Carbon sources used include sugar, L-ascorbic acid, carbon, MWCNTs, and organic surfactant cetyl trimethyl ammonium bromide CTAB), which not only increase the conductivity but also act as the reducing agent to prevent the oxidation of Fe$^{+2}$ during calcinations.$^{152, 154-156, 159, 161-163}$ Chen et al.$^{155, 163}$ studied the effect of different carbon sources, such as hydrazine, ascorbic acid, sugar, carbon black, and MWCNTs, and found that ascorbic acid gave LiFePO$_4$/C powders with the highest discharge capacity of 153 mAh g$^{-1}$ at 0.15 C. In addition, Xu et al.$^{164}$ prepared MWCNT-coated LiFePO$_4$ by hydrothermal synthesis, followed by calcination. These LiFePO$_4$-MWCNT (5 wt.%) powders showed an initial discharge capacity of 160 mAh g$^{-1}$ at 0.3 C, and the capacity fading was only 0.4% after 50 cycles. However, the agglomeration of MWCNT particles was observed at higher MWCNT concentrations. In addition to carbon, metal can be doped into LiFePO$_4$ powders to improve the conductivity. For example, Ou et al.$^{161}$ synthesized Mg-doped Li$_{0.08}$Mg$_{0.02}$FePO$_4$ by hydrothermal synthesis at 180 °C for 6 h, followed by calcination at 750 °C for 6 h.
During hydrothermal synthesis, organic surfactants are often used to improve the dispersion of precursors and increase the specific surface area of final products. Meligrana et al.\textsuperscript{159} prepared LiFePO\textsubscript{4} powders by hydrothermal synthesis and investigated the effect of organic surfactants on the morphological and electrochemical properties of LiFePO\textsubscript{4} powders. It was found that the pyrolysis of surfactants increased the material conductivity and generated a reductive environment for avoiding the oxidation of Fe\textsuperscript{+2} to Fe\textsuperscript{+3}. As a result, the cycling performance and discharge capacity increased noticeably after the addition of surfactants. Zhang et al.\textsuperscript{165} also prepared monodispersed and well-crystallized LiFePO\textsubscript{4} powders by the hydrothermal synthesis of Fe(II)–citric acid complex precursors at 180 °C and the application of isopropanol as a surfactant. It was found that the powder morphology was significantly influenced by the volume ratio of isopropanol to water. Monodispersed short rod-like LiFePO\textsubscript{4} crystals were obtained when equal volume isopropanol and water were used, and the particle size was in the range of 200 - 500 nm. However, when isopropanol was absent, column-like LiFePO\textsubscript{4} particles were obtained, and the particle size was in the range of 800 - 1100 nm.

Water temperature is one of the most important parameters for the hydrothermal synthesis process because reaction rate, ionization degree, particle size and crystalline structure of LiFePO\textsubscript{4} powders are all temperature dependent. Chen et al.\textsuperscript{154} investigated the effect of water temperature on the structure and performance of LiFePO\textsubscript{4} powders. It was found that the water temperature is directly related with the crystal structure and must be
above 170 °C to produce correct lattice parameters. With a water temperature of above 170 °C, they obtained LiFePO$_4$ powders with a discharge capacity of 145 mAh g$^{-1}$, which did not decay even after 50 cycles. Jin et al.$^{156}$ also synthesized LiFePO$_4$ powders by hydrothermal synthesis at 150, 170 and 200 °C for 10 h, followed by an additional calcination step. LiFePO$_4$ powders hydrothermally synthesized at 170 °C and calcined at 500 °C have the highest discharge capacity of 167 mAh g$^{-1}$ at 0.1 C. This value is one of the highest capacities reported for LiFePO$_4$ powders in the literature. The average particle size of these LiFePO$_4$ powders was in the range of 100 - 200 nm. Although the water temperature is typically above 170 °C, there is report on obtaining LiFePO$_4$ powders using a temperature below 170 °C. For example, Jin et al.$^{162}$ synthesized LiFePO$_4$ powders by hydrothermal synthesis at 150 °C. These LiFePO$_4$ powders were assembled into cells with solid polymer electrolyte, which showed higher discharge capacity when compared with LiFePO$_4$ cells using liquid electrolyte.

In addition to the water temperature, the flow rate of water and the concentrations of precursors have significant influence on the structure and electrochemical properties of LiFePO$_4$ powders. Xu et al.$^{164, 166}$ prepared LiFePO$_4$ powders at different water flow rates and precursor concentrations. It was found that high flow rates led to more uniform particles and higher precursor concentrations resulted in larger particle size.

Recently, supercritical hydrothermal synthesis was developed to produce LiFePO$_4$ powders. Lee et al.$^{167}$ carried out the LiFePO$_4$ synthesis under sub and supercritical water at
different temperatures, pH values, and reaction times. It was found that neutral or slightly basic pH was required for the successful synthesis of LiFePO$_4$ powders. Supercritical water gave smaller particle size ranged in the submicron scale and lower reactant concentration led to better particle size distribution. In addition, the heating time should be short in order to prevent the growth and agglomeration of particles. In a similar study, the same authors obtained LiFePO$_4$ powders by supercritical water with a capacity of 140 mAh g$^{-1}$ at 0.1 C, which is higher than that achieved by the subcritical approach.$^{168}$

So far, most LiFePO$_4$ powders were produced using the batch hydrothermal synthesis approach. However, a continuous hydrothermal synthesis route can be used for the mass production of LiFePO$_4$ powders.$^{166}$ Aimable et al.$^{169}$ prepared LiFePO$_4$ powders by continuous hydrothermal synthesis and investigated the effects of heating temperature and time on the morphological and electrochemical properties of LiFePO$_4$ powders. It was found that, with increase in temperature from subcritical to supercritical water conditions and increase in time from 6 to 12 s, well-crystalline and impurity-free LiFePO$_4$ powders were produced. Although the discharge capacities of these LiFePO$_4$ powders were only 90 mAh g$^{-1}$ at 0.01 C and 75 mAh g$^{-1}$ at 0.1 C, it can be improved with a carbon coating.
Table 1.6. Precursors used in the hydrothermal synthesis method, and particle size and electrochemical performance of the resultant LiFePO₄ powders.

<table>
<thead>
<tr>
<th>Li Precursor</th>
<th>Fe Precursor</th>
<th>P Precursor</th>
<th>Metal Dopant</th>
<th>Carbon Source</th>
<th>Molar Ratio</th>
<th>Product</th>
<th>Particle Size (nm)</th>
<th>Discharge Capacity (mA/g)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄COOLi</td>
<td>FeC₂O₄·2H₂O</td>
<td>NH₄H₂PO₄</td>
<td>Iron wire</td>
<td>Sugar</td>
<td>1:1:1</td>
<td>LiFePO₄/C</td>
<td>136 (1C)</td>
<td></td>
<td>73</td>
</tr>
<tr>
<td>LiOH·H₂O</td>
<td>(NH₄)₂Fe(SO₄)₄</td>
<td>H₂PO₄</td>
<td>Ascorbic acid</td>
<td>3:1:1</td>
<td>LiFePO₄</td>
<td>160</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiPO₄</td>
<td>Fe₅(OH)₁₀·5H₂O</td>
<td>H₂PO₄</td>
<td>Sucrose</td>
<td>1:1:1</td>
<td>LiFePO₄/C</td>
<td>1,000</td>
<td>140 (C/10)</td>
<td></td>
<td>97</td>
</tr>
<tr>
<td>LiPO₄</td>
<td>FeSO₄·7H₂O</td>
<td>Na₂PO₄</td>
<td>Sucrose (5wt.%)</td>
<td>1:1:1</td>
<td>LiFePO₄/C</td>
<td>160 (C/20)</td>
<td></td>
<td></td>
<td>117</td>
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<tr>
<td>LiOH</td>
<td>FeSO₄</td>
<td>H₂PO₄</td>
<td>Sucrose</td>
<td>3:1:1</td>
<td>LiFePO₄/C</td>
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<td>100 (0.14C)</td>
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<td>152</td>
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<td>CH₄COOLi</td>
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<td></td>
<td>Carbon gel</td>
<td>1:2:1</td>
<td>LiFePO₄/C</td>
<td>148 (C/2)</td>
<td></td>
<td></td>
<td>153</td>
</tr>
<tr>
<td>LiOH</td>
<td>FeSO₄·7H₂O</td>
<td>H₂PO₄</td>
<td>Sucrose, Ascorbic acid, CNT</td>
<td>3:1:1</td>
<td>LiFePO₄/C</td>
<td>3,000-5,000</td>
<td>145 (0.3C)</td>
<td></td>
<td>154</td>
</tr>
<tr>
<td>LiOH·H₂O</td>
<td>FeSO₄·7H₂O</td>
<td>H₂PO₄</td>
<td>Ascorbic acid, sugar</td>
<td>3:1:1</td>
<td>LiFePO₄/C</td>
<td>1,000-3,000</td>
<td>90 (0.15C)</td>
<td></td>
<td>155</td>
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<tr>
<td>LiOH·H₂O</td>
<td>FeSO₄·7H₂O</td>
<td>(NH₄)₂PO₄·3H₂O</td>
<td>Ascorbic acid</td>
<td>2:5:1:1</td>
<td>LiFePO₄</td>
<td>100-200</td>
<td>167 (C/10)</td>
<td></td>
<td>156</td>
</tr>
<tr>
<td>LiOH</td>
<td>FeSO₄·7H₂O</td>
<td>H₂PO₄</td>
<td>CTAB (C₁₀H₁₄BrN)</td>
<td>3:1:1</td>
<td>LiFePO₄/C</td>
<td>50</td>
<td>135 (C/10)</td>
<td></td>
<td>159</td>
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<tr>
<td>LiOH</td>
<td>FeSO₄·7H₂O</td>
<td>H₂PO₄</td>
<td>CTAB (C₁₀H₁₄BrN)</td>
<td>3:1:1</td>
<td>LiFePO₄/C</td>
<td>20-30</td>
<td>145 (C/10)</td>
<td></td>
<td>160</td>
</tr>
<tr>
<td>LiOH·H₂O</td>
<td>FeSO₄·7H₂O</td>
<td>H₂PO₄</td>
<td>MgSO₄</td>
<td>Glucose</td>
<td>LiMg₀.₃Fe₀.₇PO₄</td>
<td>500-1,000</td>
<td>144 (C/5)</td>
<td></td>
<td>161</td>
</tr>
<tr>
<td>LiOH·H₂O</td>
<td>FeSO₄·7H₂O</td>
<td>H₂PO₄</td>
<td>Ascorbic acid, CB</td>
<td>3:1:1</td>
<td>LiFePO₄/C</td>
<td>100-200</td>
<td>128 (C/10)</td>
<td></td>
<td>162</td>
</tr>
<tr>
<td>LiOH·H₂O</td>
<td>FeSO₄·7H₂O</td>
<td>H₂PO₄</td>
<td>Ascorbic acid w/ CNT</td>
<td>3:1:1</td>
<td>LiFePO₄/C</td>
<td>3,000-5,000</td>
<td>153 (0.15C)</td>
<td></td>
<td>163</td>
</tr>
<tr>
<td>LiOH·H₂O</td>
<td>FeSO₄</td>
<td>H₂PO₄</td>
<td>Hydrazine</td>
<td>3:1:1</td>
<td>LiFePO₄/C</td>
<td>3,000-5,000</td>
<td>80 (0.15C)</td>
<td></td>
<td>164</td>
</tr>
<tr>
<td>LiOH·H₂O</td>
<td>FeSO₄·7H₂O</td>
<td>H₂PO₄</td>
<td>MWCNTs</td>
<td>3:1:1</td>
<td>LiFePO₄/MWCNTs</td>
<td>160 (0.3C)</td>
<td></td>
<td>165</td>
<td></td>
</tr>
<tr>
<td>LiOH·H₂O</td>
<td>FeSO₄·7H₂O</td>
<td>H₂PO₄</td>
<td>Citric acid</td>
<td>3:1:1</td>
<td>LiFePO₄/C</td>
<td>200-500</td>
<td></td>
<td></td>
<td>166</td>
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<tr>
<td>LiOH</td>
<td>FeSO₄·7H₂O</td>
<td>H₂PO₄</td>
<td>3:1:1</td>
<td>LiFePO₄</td>
<td>166</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiOH</td>
<td>FeSO₄·7H₂O</td>
<td>H₂PO₄</td>
<td>3:1:1</td>
<td>LiFePO₄</td>
<td>1,000-2,000</td>
<td>167</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiPO₄</td>
<td>FeSO₄·7H₂O</td>
<td>H₂PO₄</td>
<td>1:3:2</td>
<td>LiFePO₄</td>
<td>3,000-10,000</td>
<td>168</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li₂PO₄</td>
<td>FeSO₄·7H₂O</td>
<td></td>
<td>Sucrose</td>
<td>1:1</td>
<td>LiFePO₄/C</td>
<td>100</td>
<td>140 (C/10)</td>
<td></td>
<td>168</td>
</tr>
<tr>
<td>LiOH·H₂O</td>
<td>(NH₄)₂Fe(SO₄)₄</td>
<td>H₂PO₄</td>
<td>3.75:1:1</td>
<td>LiFePO₄</td>
<td>90 (C/100)</td>
<td>169</td>
<td></td>
<td></td>
<td></td>
</tr>
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</table>
1.5.3.2. Sol-gel synthesis

Sol-gel synthesis is a low temperature, wet chemical approach, which is often used for the preparation of metal oxides or other specific compositions. Standard sol-gel synthesis involves the formation of a sol, \textit{i.e.}, a stable colloidal suspension of solid particles in a solvent, and the gelation of the sol to form a gel consisting of interconnected rigid skeleton with pores made of colloidal particles. The properties of the gel are determined by the particle size and cross-linking ratio.\textsuperscript{170-173} The gel can then be dried to form xerogel, which shows reduced volume.\textsuperscript{170-173} To obtain the final powder products, all liquids need to be removed from the surface of pores by a heat treatment carried out at elevated temperatures, which also reduces the number and connectivity of pores, known as densification.\textsuperscript{172, 173} Reaction parameters, such as temperature, time, pH, precursor, solvent, concentration, and viscosity, etc., are of importance for the formation and ultimate morphology (particle size and shape, pore size, and porosity) of the obtained powders. In sol-gel synthesis, the surfaces of the powder products are controlled from the beginning of reactions. In addition, sol-gel synthesis is low cost and does not require high processing temperature, and powders produced by this method have the advantages of precise stoichiometry control, high purity, uniform structure, and very small size.

Sol-gel synthesis has become an important means to prepare LiFePO$_4$ powders.\textsuperscript{174, 175} Dominko \textit{et al.}\textsuperscript{176} compared LiFePO$_4$ powders prepared by sol-gel and solid-state synthesis methods. Powders prepared by sol-gel synthesis have more micropores and higher capacity
(150 mAh g⁻¹ at 0.1 C) than those by solid-state synthesis (130 mAh g⁻¹ at 0.1 C). Hsu et al.¹⁷⁷ also used the sol-gel synthesis method to prepare Li₀.⁹⁹Al₀.⁰₁FePO₄ powders, and they found that the sol-gel synthesis gave powders with higher conductivity when compared with the solid-state route. The resultant specific capacity was about 150 mAh g⁻¹ at 0.025 C.

As shown in Figure 1.27, during the sol-gel synthesis of LiFePO₄ powders, precursor solutions are mixed to form sols, which are vigorously stirred at 60 – 80 °C for 12 - 24 h in order to obtain wet gel.¹⁷⁸, ¹⁷⁹ After the gelation, wet gel is dried in a vacuum or in argon atmosphere at 80 °C for 12 h in order to produce xerogel.¹⁷⁸, ¹⁷⁹ Finally, xerogel is calcined either in one or two steps at 500 – 900 °C for 3 - 30 h to produce LiFePO₄ powders.¹⁷⁷, ¹⁷⁸, ¹⁷⁹ In general, a slow heating rate during calcination causes rougher and relatively less porous structure. On the other hand, with a high heating rate, more porous structure can be obtained, which also affects the electrochemical properties of LiFePO₄ powders.¹⁷⁶

Different precursors and solvents have been used in sol-gel synthesis to produce LiFePO₄ powders (Table 1.7). The type of solvent is extremely important for the control of powder structure. Water is the most used solvent, but organic solvent can also be used in sol-gel synthesis.¹⁸⁰, ¹⁸¹ For example, Yang et al.¹⁸⁰ synthesized LiFePO₄ powders by sol-gel synthesis and used ethylene glycol as a solvent. These LiFePO₄ powders have a specific capacity of 165 mAh g⁻¹ at 0.01 C and 150 mAh g⁻¹ at both 0.2 C and 2 C, which is the indication of good rate capacity. Li et al.¹⁸² used ethanol-based sol-gel synthesis method,
which took relatively shorter synthesis time when compared with water-based sol-gel synthesis.

LiFePO$_4$ powders obtained by sol-gel synthesis often have pores in the range of 30 - 200 nm. For example, Dominko et al.$^{178}$ synthesized porous LiFePO$_4$/C powders, which have pore size between 60 and 90 nm and initial capacities of 160, 140 and 120 mAh g$^{-1}$ at 0.05 C, 0.5 C and 5 C, respectively. During the formation of porous LiFePO$_4$ powders, the agglomeration tendency can be reduced noticeably by using surfactants.$^{183}$ Choi et al.$^{183}$ prepared porous LiFePO$_4$ powder with a narrow particle size distribution (100 – 300 nm) by employing lauric acid as a surfactant and achieved discharge capacities of 123, 157 and 170 mAh g$^{-1}$ at 10 C, 1 C and 0.1 C, respectively. The presence of pores not only increases the specific surface area but also shortens the transportation pathway of lithium inside the material. The porous structure is useful especially if the pores are covered by an electrical conductor.$^{177-180, 183}$

The most common approach to create an electrically conducting coating on the pore surface is by directly adding a carbon source during sol-gel synthesis.$^{178, 184, 185}$ The carbon source not only improves the electrical conductivity of LiFePO$_4$ powders, but also contributes to the formation of the porous structure through the degradation and pyrolysis processes. In addition, the presence of carbon source enhances the uniform growth of LiFePO$_4$ particles with relatively small sizes by decreasing the aggregation tendency.$^{177, 180}$

$^{184}$ The thickness of the carbon layer can be as low as 1 - 2 nm in the form of amorphous
carbon or graphene-rich phase. Sucrose and citric acid are the most commonly used carbon sources for the sol-gel method. Kim et al. used sucrose and citric acid as the carbon sources to synthesize porous LiFePO₄/C powders, in which the pore surfaces are covered by a graphene-rich carbon layer of 2 - 4 nm thick. It was found that these porous LiFePO₄/C powders showed high discharge capacities of 153 and 94 mAh g⁻¹ at 0.1 C and 5 C, respectively, which are probably caused by the large surface areas of the porous structures. In addition to sucrose and citric acid, other carbon sources can be used. For example, Li et al. used PEG and D-fructose as the carbon source and obtained porous LiFePO₄/C powders with the highest specific capacities of 130.9 and 157.7 mAh g⁻¹ at 1C and 0.2 C, respectively. One advantage of the sol-gel synthesis method is the relatively easy control of carbon coating thickness. Dominko et al. synthesized LiFePO₄/C powders with different carbon layer thicknesses ranging from 1 to 10 nm, which are among the lowest values in the literature. These LiFePO₄/C powders have high discharge capacity of 150 mAh g⁻¹ at 0.2 C.

In addition to carbon coating, metal dopants can also be added to modify the structure and electrochemical performance of LiFePO₄ powders. Wang et al. doped Mg, Zr, and Ti metals into the crystal structure of LiFePO₄ powders and they found that the Ti doping led to the highest discharge capacity, which is around 160 mAh g⁻¹ at 0.125 C. Lee et al. also prepared sulfur-doped LiFePO₃.98S₀.03 powders by sol-gel synthesis in order to enhance the performance of the Li/LiFePO₄ cells at high temperatures. They obtained good discharge
capacities of around 155 mAh g\(^{-1}\) at all temperatures because of the improved stability caused by the substitution of O\(^2\) with S\(^2\).
Table 1.7. Precursors used in the sol-gel synthesis method, and particle size and electrochemical performance of the resultant LiFePO$_4$ powders.

<table>
<thead>
<tr>
<th>Li Precursor</th>
<th>Fe Precursor</th>
<th>P Precursor</th>
<th>Metal Dopant</th>
<th>Solvent</th>
<th>Carbon Source</th>
<th>Molar Ratio</th>
<th>Product</th>
<th>Pore* or Particle Size (nm)</th>
<th>Discharge Capacity (mAh g$^{-1}$)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiOH·H$_2$O</td>
<td>Fe(NO$_3$)$_3$·9H$_2$O</td>
<td>H$_3$PO$_4$</td>
<td>MeOH</td>
<td>Ascorbic acid</td>
<td>1:1:1</td>
<td>LiFePO$_4$/C</td>
<td>100,000</td>
<td>80 (C/5)</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>Li$_3$PO$_4$</td>
<td>FeC$_6$H$_5$O$_7$·nH$_2$O</td>
<td>H$_3$PO$_4$</td>
<td>Deionized water</td>
<td>1:3:2</td>
<td>LiFePO$_4$</td>
<td>116</td>
<td>117</td>
<td>81</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li$_3$PO$_4$</td>
<td>C$_3$H$_7$FeO$_3$</td>
<td>H$_3$PO$_4$</td>
<td>Deionized water</td>
<td>1:3:2</td>
<td>Porous LiFePO$_4$/C</td>
<td>*90</td>
<td>150 (C/10)</td>
<td>176</td>
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<td></td>
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<td>LiNO$_3$</td>
<td>Iron powder</td>
<td>NH$_2$H$_2$PO$_4$</td>
<td>Al(NO$_3$)$_3$·6H$_2$O</td>
<td>Deionized water</td>
<td>Citric acid</td>
<td>0.99:1:0:0.01</td>
<td>Li$<em>{0.99}$Al$</em>{0.01}$FePO$_4$/C</td>
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<td>150 (C/40)</td>
<td>177</td>
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<td>Li$_3$PO$_4$</td>
<td>C$_3$H$_7$FeO$_3$</td>
<td>H$_3$PO$_4$</td>
<td>Deionized water</td>
<td>1:3:2</td>
<td>Porous LiFePO$_4$/C</td>
<td>*60-90</td>
<td>160 (C/10)</td>
<td>178</td>
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<td></td>
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<tr>
<td>Li$_3$PO$_4$</td>
<td>FeC$_6$O$_7$·2H$_2$O</td>
<td>NH$_2$H$_2$PO$_4$</td>
<td>Deionized water</td>
<td>1:1:1</td>
<td>Porous LiFePO$_4$/C</td>
<td>*9.1</td>
<td>128 (C/10)</td>
<td>179</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li$_3$PO$_4$</td>
<td>FeC$_6$O$_7$·2H$_2$O</td>
<td>NH$_2$H$_2$PO$_4$</td>
<td>Deionized water</td>
<td>1:1:1</td>
<td>Porous LiFePO$_4$/C</td>
<td>*6.1</td>
<td>153 (C/10)</td>
<td>179</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li(COOCH$_3$)$_2$·H$_2$O</td>
<td>Fe(COOCH$_3$)$_2$</td>
<td>H$_3$PO$_4$</td>
<td>Ethylene glycol</td>
<td>Ethylene glycol</td>
<td>1:1:1</td>
<td>LiFePO$_4$/C</td>
<td>200-300</td>
<td>165 (C/100)</td>
<td>180</td>
<td></td>
</tr>
<tr>
<td>LiNO$_3$</td>
<td>FeC$_6$O$_7$·2H$_2$O</td>
<td>NH$_2$H$_2$PO$_4$</td>
<td>Deionized water</td>
<td>Ethylene glycol</td>
<td>1:1:1</td>
<td>LiFePO$_4$/C</td>
<td>155 (C/10)</td>
<td>181</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiCl·H$_2$O</td>
<td>FeCl$_2$·4H$_2$O</td>
<td>H$_3$PO$_4$</td>
<td>Ethanol</td>
<td>1:1:1</td>
<td>LiFePO$_4$</td>
<td>116 (C/5)</td>
<td>116</td>
<td>182</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiCl·H$_2$O</td>
<td>FeCl$_2$·4H$_2$O</td>
<td>H$_3$PO$_4$</td>
<td>Ethanol</td>
<td>1:1:1</td>
<td>Porous LiFePO$_4$/C</td>
<td>145 (C/5)</td>
<td>182</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiCl·H$_2$O</td>
<td>FeCl$_2$·4H$_2$O</td>
<td>H$_3$PO$_4$</td>
<td>Ethanol</td>
<td>1:1:1</td>
<td>Porous LiFePO$_4$/C</td>
<td>157.7 (C/5)</td>
<td>182</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiCl·H$_2$O</td>
<td>FeCl$_2$·4H$_2$O</td>
<td>H$_3$PO$_4$</td>
<td>Ethanol</td>
<td>1:1:1</td>
<td>Porous LiFePO$_4$/C</td>
<td>100-200</td>
<td>137 (C/5)</td>
<td>182</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li(COOCH$_3$)$_2$·2H$_2$O</td>
<td>FeCl$_2$·4H$_2$O</td>
<td>P$_2$O$_5$</td>
<td>Ethanol</td>
<td>Lauric acid</td>
<td>1:1:1</td>
<td>LiFePO$_4$</td>
<td>100-300</td>
<td>170 (C/10)</td>
<td>183</td>
<td></td>
</tr>
<tr>
<td>Li(COOCH$_3$)$_2$·2H$_2$O</td>
<td>FeCl$_2$·4H$_2$O</td>
<td>P$_2$O$_5$</td>
<td>Ethanol</td>
<td>Lauric acid</td>
<td>1:1:1</td>
<td>LiFePO$_4$</td>
<td>500-3,000</td>
<td>146 (C/10)</td>
<td>183</td>
<td></td>
</tr>
<tr>
<td>Li₃PO₄</td>
<td>C₆H₅FeO₂</td>
<td>H₃PO₄</td>
<td>Deionized water</td>
<td>Hydroxy ethyl cellulose</td>
<td>1:3:2</td>
<td>Porous LiFePO₄/C</td>
<td>500-20,000</td>
<td>140 (C/2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------</td>
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</tr>
<tr>
<td>Li₃PO₄</td>
<td>C₆H₅FeO₂</td>
<td>H₃PO₄</td>
<td>Deionized water</td>
<td>Hydroxy ethyl cellulose</td>
<td>1:3:2</td>
<td>Porous LiFePO₄/C</td>
<td>500-20,000</td>
<td>150 (C/5)</td>
<td></td>
<td></td>
</tr>
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<td>LiOH·H₂O</td>
<td>FeC₂O₄·2H₂O</td>
<td>NH₄H₂PO₄</td>
<td>Deionized water</td>
<td>Polyacrylic acid, Citric acid</td>
<td>1:1:1</td>
<td>LiFePO₄</td>
<td>160-165(C/8)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiOH·H₂O</td>
<td>FeC₂O₄·2H₂O</td>
<td>NH₄H₂PO₄</td>
<td>Deionized water</td>
<td>Polyacrylic acid, Citric acid</td>
<td>1:0.99:1:0.01</td>
<td>LiMg₀.01Fe₀.99PO₄</td>
<td>160-165(C/8)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiOH·H₂O</td>
<td>FeC₂O₄·2H₂O</td>
<td>NH₄H₂PO₄</td>
<td>Deionized water</td>
<td>Polyacrylic acid, Citric acid</td>
<td>1:0.99:1:0.01</td>
<td>LiZr₀.01Fe₀.99PO₄</td>
<td>160-165(C/8)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiOH·H₂O</td>
<td>FeC₂O₄·2H₂O</td>
<td>NH₄H₂PO₄</td>
<td>Deionized water</td>
<td>Polyacrylic acid, Citric acid</td>
<td>1:0.99:1:0.01</td>
<td>LiTl₀.01Fe₀.99PO₄</td>
<td>160-165(C/8)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li₃PO₄</td>
<td>C₆H₅FeO₂</td>
<td>H₃PO₄</td>
<td>Deionized water</td>
<td>Citric acid</td>
<td>1:3:2</td>
<td>Porous LiFePO₄/C</td>
<td>*50</td>
<td>120 (1C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiCO₃</td>
<td>Fe(NO₃)₃·9H₂O</td>
<td>NH₄H₂PO₄</td>
<td>Deionized water</td>
<td>Ascorbic acid</td>
<td>1:1:1</td>
<td>LiFePO₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiOH·H₂O</td>
<td>Fe(NO₃)₃·9H₂O</td>
<td>H₃PO₄</td>
<td>Deionized water</td>
<td>Ascorbic acid</td>
<td>1:1:1</td>
<td>LiFePO₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li(COOCH₃)₂</td>
<td>Fe(COOCH₃)₂</td>
<td>H₃PO₄</td>
<td>DMF</td>
<td>1:05:1:1</td>
<td>LiFePO₄</td>
<td>5,000</td>
<td>145 (C/2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li(COOCH₃)₂</td>
<td>Fe(COOCH₃)₂</td>
<td>H₃PO₄</td>
<td>Ethylene glycol</td>
<td>Functionalized CNF by HNO₃</td>
<td>1:1:1</td>
<td>LiFePO₄/CNF</td>
<td>200</td>
<td>120 (C/2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li(COOCH₃)₂</td>
<td>Fe(COOCH₃)₂</td>
<td>H₃PO₄</td>
<td>Ethylene glycol</td>
<td>Functionalized CNF by HNO₃</td>
<td>1:1:1</td>
<td>LiFePO₄/CNF</td>
<td>200</td>
<td>120 (C/2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiOH·H₂O</td>
<td>Fe(NO₃)₃·9H₂O</td>
<td>H₃PO₄</td>
<td>Deionized water</td>
<td>Ascorbic acid</td>
<td>1:1:1</td>
<td>LiFePO₄/C</td>
<td>500-1,000</td>
<td>110 (C/2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiOH·H₂O</td>
<td>Fe(NO₃)₃·9H₂O</td>
<td>H₃PO₄</td>
<td>Deionized water</td>
<td>Ascorbic acid</td>
<td>1:1:1</td>
<td>LiFePO₄/C</td>
<td>350</td>
<td>165 (3C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiOH·H₂O</td>
<td>Fe(NO₃)₃·9H₂O</td>
<td>H₃PO₄</td>
<td>Deionized water</td>
<td>Ascorbic acid</td>
<td>1:1:1</td>
<td>LiFePO₄/C</td>
<td>110 (C/5)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiOH·H₂O</td>
<td>Fe(NO₃)₃·9H₂O</td>
<td>H₃PO₄</td>
<td>Metal powder (Co, Ag)</td>
<td>Ascorbic acid</td>
<td>1:1:1</td>
<td>LiFePO₄/C</td>
<td>140 (C/5)</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>
1.5.3.3. Spray pyrolysis

Spray pyrolysis is an important method for the preparation of ultrafine powders, and it is based on the generation of droplets in a continuous way from a solution containing precursor colloidal particles. Droplets can be generated by using different techniques, such as ultrasonic transduction and peristaltic pump. In spray pyrolysis, the generation of droplets is a key step because the droplets act as the nucleation centers and eventually evolve to well-crystallized, dense, and pure particles. Powders produced by this method have small particle size (< 1 µm), narrow size distribution (in the range of 1 – 2 µm), large surface area, and high purity. All these properties are desirable for achieving high electrochemical performance for LiFePO4 powders, and hence spray pyrolysis method is becoming an important alternative approach for producing LiFePO4 powders. Table 1.8 shows the precursors used in the spray pyrolysis method and the particle size and discharge capacity of the resultant LiFePO4 powders.

The spray pyrolysis of LiFePO4 powders typically starts with the pumping (or spraying) of a solution of mixed precursors into a pyrolysis furnace (around 400 – 600 °C) in the droplet form by a carrier gas (Figure 1.27). Collected precursor powders are then calcined at temperatures around 700 – 800 °C. Jugovic et al. compared LiFePO4 powders prepared by solid state synthesis and spray pyrolysis, and found that LiFePO4 powders by spray pyrolysis have smaller particle size and present spherical morphology without agglomeration. However, powders by solid-state synthesis are formed of larger and
nonspherical particles with apparent agglomeration. In addition, powders prepared by solid-state synthesis show well crystallized structure as single-phase phospho-olivines, whereas those prepared by spray pyrolysis have olivine phase with small portion of other phases such as lithium carbon and iron carbon, which lead to higher electrical conductivity.

Like many other methods, carbon sources can be added during spray pyrolysis, and the resultant LiFePO₄/C powders not only have higher electrical conductivity, but also have smaller particle size, which increases the specific surface area of the powders.¹⁹⁸,²⁰⁰ Bewlay et al.¹⁹⁹ used sucrose as a carbon source to prepare LiFePO₄/C powders, which had an average diameter of 300 nm and showed a conductivity from 10⁻⁷ to 10⁻¹ S cm⁻¹, depending on the amount of the carbon source added in the precursor solution. Konarova et al.²⁰⁰ also prepared LiFePO₄ and LiFePO₄/C powders by the spray pyrolysis method. While LiFePO₄ powders had low discharge capacity of around 100 mAh g⁻¹ at 0.1 C, LiFePO₄/C powders showed 140 mAh g⁻¹ at 0.1 C and 84 mAh g⁻¹ at 5 C, respectively, with small capacity fading during cycling. Ju et al.¹⁹⁷ also reported fine, spherical LiFePO₄/C powders with charge capacities between 108 - 136 mAh g⁻¹, depending on the size and amount of the carbon. Capacities and cycling performance of LiFePO₄/C powders are reported to be improved by preparing nano-sized particles. It must be noted that, when a carbon source is added, the carbon content in the final LiFePO₄/C product needs to be carefully controlled because, if the carbon content is too high, the discharge capacity may decrease due to either reduced LiFePO₄ content²⁰³ or dominant barrier behavior of the thick carbon layer.¹⁸⁵,²⁰⁰ Yang et
al. prepared non-agglomerated, smooth LiFePO$_4$/C powders with carbon evenly distributed. When the carbon content is 15 wt %, the LiFePO$_4$/C powders have the highest discharge capacity of 124 mAh g$^{-1}$ at 0.1 C.

Metal dopants have also been used in the spray pyrolysis method to improve the performance of LiFePO$_4$ powders. For example, Teng et al. synthesized Mg-doped LiFePO$_4$/C powders, which have an average particle size between 1 and 2 µm and a conductivity $10^4$ greater than that of pure LiFePO$_4$. These powders have a capacity of 132 mAh g$^{-1}$ at 0.1 C and exhibit lower capacity decay when compared with undoped LiFePO$_4$/C powders. Wang et al. also prepared Mg-doped LiFePO$_4$ powders using spray pyrolysis and achieved $10^4$ times higher conductivity than pure LiFePO$_4$ powders.

The spray pyrolysis method can also be combined with wet or dry ball-milling techniques in order to increase the specific surface area and discharge capacity of the resultant LiFePO$_4$ powders. Konarova et al. produced LiFePO$_4$ powders with average diameter less than 100 nm by the combination of spray pyrolysis and wet ball-milling. These powders have discharge capacities of 163 mAh g$^{-1}$ at 0.1 C and 100 mAh g$^{-1}$ at 10 C, respectively. The same authors also reported the preparation of LiFePO$_4$/C powders with diameters ranging from 300 to 1000 nm by the combination of spray pyrolysis and planetary ball-milling, and achieved a discharge capacity of 158 mAh g$^{-1}$ at 0.1 C.
Table 1.8. Precursors used in the spray pyrolysis method, and particle size and electrochemical performance of the resultant LiFePO₄ powders.

<table>
<thead>
<tr>
<th>Li Precursor</th>
<th>Fe Precursor</th>
<th>P Precursor</th>
<th>Metal Dopant</th>
<th>Solvent</th>
<th>Carbon Source</th>
<th>Molar Ratio</th>
<th>Product</th>
<th>Particle Size (nm)</th>
<th>Discharge Capacity (mAh g⁻¹)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNO₃</td>
<td>FeSO₄</td>
<td>H₃PO₄</td>
<td></td>
<td>Deionized water</td>
<td>Sucrose</td>
<td>LiFePO₄/C</td>
<td></td>
<td>1,000-2,000</td>
<td>132 (C/10)</td>
<td>104</td>
</tr>
<tr>
<td>LiNO₃</td>
<td>Fe(NO₃)₃·9H₂O</td>
<td>H₃PO₄</td>
<td>Mg(NO₃)₂·6H₂O</td>
<td>Deionized water</td>
<td>White sugar 40 wt%</td>
<td>LiFeₐₓMgₐₓPO₄/C</td>
<td>1:0.9:1:0.1</td>
<td></td>
<td>1,000-2,000</td>
<td>195</td>
</tr>
<tr>
<td>Li₂CO₃</td>
<td>FeC₂O₄·2H₂O</td>
<td>NH₃H₂PO₄</td>
<td>Mg(C₂H₃O₂)₄·4H₂O</td>
<td>Deionized water</td>
<td>1-x:1:1:x</td>
<td>Li₁ₓFeMgₓPO₄</td>
<td>1,000-2,000</td>
<td></td>
<td>196</td>
<td></td>
</tr>
<tr>
<td>LiNO₃</td>
<td>Fe(NO₃)₃·9H₂O</td>
<td>H₃PO₄</td>
<td></td>
<td>Deionized water</td>
<td>Ascorbic acid, white sugar</td>
<td>LiFePO₄/C</td>
<td></td>
<td>1,000-2,000</td>
<td>124 (C/10)</td>
<td>198</td>
</tr>
<tr>
<td>LiCO₃</td>
<td>FeC₂O₄·2H₂O</td>
<td>NH₃H₂PO₄</td>
<td></td>
<td>Deionized water</td>
<td>Sucrose (C₁₂H₂₂O₁₁)</td>
<td>LiFePO₄/C</td>
<td></td>
<td>300</td>
<td>199</td>
<td></td>
</tr>
<tr>
<td>Li(HCOO)·H₂O</td>
<td>FeCl₂·4H₂O</td>
<td>H₃PO₄</td>
<td></td>
<td>Deionized water</td>
<td>1:1:1</td>
<td>LiFePO₄</td>
<td></td>
<td>100 (C/10)</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>Li(HCOO)·H₂O</td>
<td>FeCl₂·4H₂O</td>
<td>H₃PO₄</td>
<td></td>
<td>Deionized water</td>
<td>Citric acid</td>
<td>LiFePO₄/C</td>
<td></td>
<td>1,000-3,000</td>
<td>140 (C/10)</td>
<td>200</td>
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<tr>
<td>Li(HCOO)·H₂O</td>
<td>FeCl₂·4H₂O</td>
<td>H₃PO₄</td>
<td></td>
<td>Deionized water</td>
<td>Acetylene black</td>
<td>LiFePO₄/C</td>
<td></td>
<td>58</td>
<td>163 (C/10)</td>
<td>201</td>
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<tr>
<td>Li(HCOO)·H₂O</td>
<td>FeCl₂·4H₂O</td>
<td>H₃PO₄</td>
<td></td>
<td>Deionized water</td>
<td>Acetylene black</td>
<td>LiFePO₄/C</td>
<td></td>
<td>300-1,000</td>
<td>158 (C/10)</td>
<td>202</td>
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</tbody>
</table>
1.5.3.4. Co-precipitation

Co-precipitation is another solution-based method, which is easy to control and can lead to well-crystallized powders with high purity and small particle size. In that method, lithium and phosphate compounds in mixed precursor solutions are co-precipitated by controlling the pH values. The co-precipitated slurries are then filtered, washed, and dried under N₂ atmosphere. During that process, dried precursors may form amorphous LiFePO₄. Crystalline LiFePO₄ powders are obtained by carrying out the calcination at 500 – 800 °C for 12h under N₂ or argon flow. The typical synthesis route for the co-precipitation method is shown in Figure 1.27 and precursors used in this method are shown in Table 1.9. Depending on the precursors and other processing conditions, the particle sizes of the synthesized LiFePO₄ powders can range from 100 nm to several microns. For example, Zheng et al. prepared pure crystalline LiFePO₄ powders by calcining an amorphous co-precipitated LiFePO₄ at 500 °C. These powders have a homogenously distributed particle size ranging from 100 and 200 nm, and their discharge capacity is 166 mAh g⁻¹ at 0.1 C. In addition to particle size, the particle morphology can also be controlled using the co-precipitation method. Arnold et al. prepared flat, rhombus-shaped LiFePO₄ powders in the submicron range by an aqueous co-precipitation method. These pure and well-crystallized LiFePO₄ powders have a high discharge capacity of 160 mAh g⁻¹ at 0.05 C.

The structure and performance of LiFePO₄ powders can be improved by introducing carbon source or metal dopant into the co-precipitation process. For example, Ding et al.
prepared LiFePO$_4$/graphene composite powders by directly adding graphene during co-
precipitation, and observed the restacking of graphene sheets because the van der Waals
forces during synthesis caused a decrease in surface area of graphene. The resultant
LiFePO$_4$/graphene powders have an average particle size of around 100 nm and a discharge
capacity of 160 mAh g$^{-1}$ at 0.2 C rate. Li et al.$^{207}$ prepared spherical shaped, sub-micron sized
Ti-doped LiFePO$_4$ powders by the co-precipitation method. Ti(SO$_4$)$_2$ was used as the
titanium dopant. It was found that 3%-Ti-doped powders exhibited a good discharge capacity
of 150 mAh g$^{-1}$ at 0.1 C with good cycling performance.

Co-precipitation can also be combined with other methods to produced LiFePO$_4$ powders
with controlled structures and performance. Chang et al.$^{208}$ prepared high-density LiFePO$_4$/C
powders by the solid-state synthesis of FePO$_4$ (1.56 g cm$^{-3}$), which was obtained by using the
co-precipitation method supported with high-pressure filtering and two-step drying at 80°C.
The tap-density of the obtained LiFePO$_4$/C powders was 1.80 g cm$^{-3}$ when the carbon content
was 7 wt %. The initial volumetric and gravimetric discharge capacities were 300.6 mAh cm$^{-3}$
and 167 mAh g$^{-1}$, respectively, at 0.1 C.
Table 1.9. Precursors used in the co-precipitation and microemulsion drying methods, and particle size and electrochemical performance of the resultant LiFePO₄ powders.

<table>
<thead>
<tr>
<th>Method</th>
<th>Li Precursor</th>
<th>Fe Precursor</th>
<th>P Precursor</th>
<th>Solvent</th>
<th>Carbon Source</th>
<th>Molar Ratio</th>
<th>Product</th>
<th>Particle Size (nm)</th>
<th>Discharge Capacity (mAh g⁻¹)</th>
<th>Ref</th>
</tr>
</thead>
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<tr>
<td>Co-precipitation</td>
<td>LiOH</td>
<td>Ferrous ions</td>
<td>H₃PO₄</td>
<td>Deionized water</td>
<td></td>
<td></td>
<td>LiFePO₄</td>
<td></td>
<td></td>
<td>97</td>
</tr>
<tr>
<td>Co-precipitation</td>
<td>Li₃PO₄</td>
<td>Fe₃(PO₄)₂·5H₂O</td>
<td>Deionized</td>
<td></td>
<td></td>
<td></td>
<td>LiFePO₄</td>
<td>&lt;1,000</td>
<td>160 (C/20)</td>
<td>204</td>
</tr>
<tr>
<td>Co-precipitation</td>
<td>Li₂CO₃</td>
<td>FeSO₄·7H₂O</td>
<td>H₃PO₄</td>
<td>Deionized water</td>
<td>C₄H₈H₂·2H₂O</td>
<td>1:1:1</td>
<td>LiFePO₄</td>
<td>100-200</td>
<td>166 (C/10)</td>
<td>205</td>
</tr>
<tr>
<td>Co-precipitation</td>
<td>LiOH</td>
<td>(NH₄)₂Fe(SO₄)₂·6H₂O</td>
<td>NH₄H₂PO₄</td>
<td>Deionized water</td>
<td>Natural graphite</td>
<td>1:1:1</td>
<td>LiFePO₄/C</td>
<td></td>
<td></td>
<td>206</td>
</tr>
<tr>
<td>Co-precipitation</td>
<td>Li₂CO₃</td>
<td>Fe(NO₃)₃·9H₂O</td>
<td>H₃PO₄</td>
<td>Deionized water</td>
<td>Glucose</td>
<td>1:1:1</td>
<td>LiFePO₄/C</td>
<td>2,000-4,000</td>
<td>167 (C/10)</td>
<td>208</td>
</tr>
<tr>
<td>Emulsion-Drying</td>
<td>LiNO₃</td>
<td>Fe(NO₃)₃·9H₂O</td>
<td>(NH₄)₂HPO₄</td>
<td>Deionized water</td>
<td>Carbon B1 (40%)</td>
<td>1:1:1</td>
<td>LiFePO₄/C</td>
<td>1,000</td>
<td>133 (C/8.5)</td>
<td>209</td>
</tr>
<tr>
<td>Emulsion-Drying</td>
<td>LiNO₃</td>
<td>Fe(NO₃)₃·9H₂O</td>
<td>(NH₄)₂HPO₄</td>
<td>Deionized water</td>
<td></td>
<td>1:1:1</td>
<td>LiFePO₄</td>
<td>1,000</td>
<td>121 (C/8.5)</td>
<td>209</td>
</tr>
<tr>
<td>Emulsion-Drying</td>
<td>LiNO₃</td>
<td>Fe(NO₃)₃·9H₂O</td>
<td>(NH₄)₂HPO₄</td>
<td>Deionized water</td>
<td>Karosene:Tween85</td>
<td>1:1:1</td>
<td>LiFePO₄/C</td>
<td>&lt;1,000</td>
<td>125(C/8.5)</td>
<td>210</td>
</tr>
<tr>
<td>Emulsion-Drying</td>
<td>LiOH</td>
<td>(NH₄)₂Fe(SO₄)₂</td>
<td>H₃PO₄</td>
<td>Octane, Butyl alcohol</td>
<td>Sugar</td>
<td>3:1:1</td>
<td>LiFePO₄/C</td>
<td>90</td>
<td>163 (C/10)</td>
<td>211</td>
</tr>
</tbody>
</table>
1.5.3.5. Microemulsion drying

LiFePO$_4$ powders can also be prepared by the drying of microemulsion solutions, which are thermodynamically stable liquid mixtures consisting of water, oil, and emulsifying agent that stabilizes the microemulsions. During the microemulsion drying process, microemulsions act as microreactors for the synthesis of LiFePO$_4$ powders. The type and property of the microemulsions are depended on the amount of oil and water, type and amount of emulsifying agent, and process temperature, etc. As shown in Figure 1.27, the microemulsion drying process of LiFePO$_4$ powders starts with the preparation of aqueous precursor solutions based on the stoichiometric ratios. The aqueous phase is mixed intensively with an oily phase consisting of hydrocarbons such as Kerosene. The obtained microemulsions are dried between 300 and 400 °C, during which extensive weight loss can be observed due to the evaporation of water and pyrolysis of organic hydrocarbons. It was reported that little amount of crystalline olivine LiFePO$_4$ starts to form during drying. However, in most cases, dried microemulsions need to be calcined at 650 – 850 °C under argon flow for 12 h. The optimum calcination temperature is reported to be around 750 °C. Higher calcination temperature might result in increased particle size. The microemulsion drying process is of importance for LiFePO$_4$ synthesis because the formation of pure, fine powders is facilitated by the atomic scale, homogeneous distribution of reactants in microemulsions from the beginning.
During microemulsion drying, the particle growth is directly restricted by the size of the droplets in the emulsions. As a result, the particle size and morphology are affected by many factors such as solution concentration, droplet size, stirring power, and surfactant. Particle sizes and discharge capacities of LiFePO$_4$ powders produced by microemulsion drying are shown in Table 1.9. Myung et al.$^{210}$ used the microemulsion drying method (drying at 300 °C and calcination at 750 °C) to prepare LiFePO$_4$/C powders, which have an average particle size of 1 µm. Good discharge capacity (around 125 mAh g$^{-1}$ at 0.117 C and 25 °C) and good electrical conductivity ($10^{-4}$ S cm$^{-1}$) were obtained for the LiFePO$_4$/C powders due to the atomic level mixing of precursors and carbon source. Smaller particle size can be obtained using the microemulsion drying method. For example, Xu et al.$^{211}$ prepared LiFePO$_4$/C powders by using CTAB and PEG in emulsions to control the particle size and using sugar as the carbon source. LiFePO$_4$/C powders calcined at 600 °C exhibited 90 nm average particle size and very good discharge capacity of 163 mAh g$^{-1}$ at 0.1 C. Cho et al.$^{209}$ prepared pristine LiFePO$_4$ and LiFePO$_4$/C powders using the same method. Discharge capacities of 121 and 133 mAh g$^{-1}$ at 0.117 C with excellent cycle stability were obtained for LiFePO$_4$ and LiFePO$_4$/C powders, respectively.
1.5.4. Other methods

There are other methods that can be used to produce LiFePO$_4$ powders in addition to the previously mentioned approaches. Among these methods, template synthesis,$^3$ polyol process,$^{218}$ in-situ polymerization restriction method,$^{219}$ electrospinning,$^{220}$ and solid-state synthesis with controlled off-stoichiometry$^{221}$ stand out because they lead to LiFePO$_4$ powders with desired structure and fast charge/discharge behavior. In-situ polymerization restriction and electrospinning methods are given in Figure 1.28 and Figure 1.29, respectively.

![Schematic representation of in-situ polymerization restriction method.](image)

Figure 1.28. Schematic representation of in-situ polymerization restriction method.$^{219}$

In addition, a molten salt synthesis method was used to accelerate the crystallization process and help form spherical powders with increased tap density.$^{222}$ Other methods that
have been used to produce LiFePO$_4$ powders include ceramic granulation,$^{223}$ freeze-drying,$^{224}$ sonochemical synthesis,$^{104,212}$ and rheological synthesis.$^{225}$

![Figure 1.29. (a) Model image of the triaxial nanowire with a MWCNT core column, and the two layer shells and corresponding (b) SEM and (c) TEM images.][1]

Recently, a few research groups are working on synthesizing LiFePO$_4$ films that have comparable electrochemical performance to powders. For example, LiFePO$_4$$^{226-229}$ thin films with different thicknesses, such as 35 nm,$^{228}$ 50 nm,$^{226}$ and 300 nm,$^{227,229}$ have been produced by using pulsed laser deposition method. Another method to produce LiFePO$_4$ thin films is radio frequency magnetron sputtering, which can be used to obtain submicron size film thickness.$^{230}$
CHAPTER 2. OBJECTIVES

Current positive electrodes (cathodes) are constructed by binding active cathode materials using a polymer binder, such as polyvinylidene fluoride (PVDF) or polytetrafluoroethylene (PTFE). Non-active carbon black particles are added to enhance the electrical conductivity. The presence of polymer binder in electrodes separates many active materials from the electrolyte, which reduces the effective electrode-electrolyte interface area and causes slow electrode reaction kinetics, especially at high current densities. In this research, a combination of electrospinning and sol-gel techniques is used to fabricate binder-free electrospun cathodes for lithium-ion batteries.

Electrospun nanofibers are promising electrode materials since they have shorter Li-diffusion pathway relative to the commonly employed powder materials with faster intercalation kinetics due to their high surface area to volume ratio. Our goal was to produce one-dimensional nanostructured materials with high-electrochemical performance using the electrospinning technique, which provides a unique approach to prepare versatile nanofibers from a rich variety of materials including polymers, composites, and ceramics. This work focused on the fabrication of one-dimensional cathode nanofibers with short-diffusion distance and high-lithium diffusion coefficient. Such nanofibers would also exhibit excellent charge/discharge rate capability with extended cycle performance. To this end, PAN was
used as both electrospinning media and conductive carbon source; LiFePO₄ were in-situ synthesized in the matrix and used as active material of the electrode.

The **first objective** of this research was to fabricate LiFePO₄/C composite nanofibers as cathode materials for rechargeable LIBs and to determine the effect of fabrication parameters including carbon amount, carbon coating thickness, stabilization and carbonization temperature, calcination/carbonization time, *etc.* Electrochemically active LiFePO₄ particles were in-situ synthesized and coated by carbon matrix. Unlike in previous studies such as mixing or coating LiFePO₄ with a conducting material, here, conductive coating and LiFePO₄ formation took place at the same time during heat treatment, which ensured nano-scale carbon coating on the particle surface and maximizes the LiFePO₄–carbon interface. In this work, LiFePO₄/C composite nanofibers with different carbon contents were fabricated, and results are discussed in Chapter 4.

Amorphous nature of the carbon nanofiber matrix limits the electrical conductivity of the electrode, leading to unsatisfactory rate capability performance. In order to overcome this obstacle, the electrode conductivity can be improved by using conductive additives, *i.e.*, carbon black, CNTs, graphene sheets, conductive polymers or metal-ions. Our **second objective** was, therefore, to enhance the conductivity of LiFePO₄/C composite nanofibers by dispersing conductive additives without damaging the network-like structure of electrospun web. For this aim, CNTs and graphene sheets are used. CNTs and graphene sheets formed conducting bridges between LiFePO₄ particles and increased the electrical conductivity of
the system. In addition, CNT- and graphene-containing nanofiber structure restricted the particle agglomeration of LiFePO$_4$ during synthesis, and this further shortened the charge transfer distance and led to increased lithium diffusion coefficient. In this work, CNT- and graphene-loaded LiFePO$_4$/C nanofibers were fabricated, and results are discussed in Chapters 5 and 6.

Although different modifications were carried out in order to increase the electrochemical capacity of LiFePO$_4$, it is not sufficient enough for high energy and high-power required systems such as electrical vehicles. Our **third objective** was to synthesize high capacity cathode materials. Since mixed form of Li-rich layered metal oxides (Li-Ni-Mn-Co) show noticeable improvement in the capacity and cycling behavior; various $x$Li$_2$MnO$_3$·(1-$x$)LiCo$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$ ($x$=0.1, 0.2, 0.3, 0.4, 0.5) composite cathode materials were prepared by a single-step sol-gel route and results are discussed in Chapter 7. This study is of importance in terms of optimization of the process, easy synthesis and industry scalability.
CHAPTER 3. OVERALL EXPERIMENTAL SECTION

3.1. Chemicals and reagents

Polyacrylonitrile (PAN, 150,000 g mol\(^{-1}\)), was purchased from Pfaltz & Bauer Inc. Lithium acetate (LiCOOCH\(_3\)), phosphoric acid (H\(_3\)PO\(_4\)), iron (II) acetate (Fe(COOCH\(_3\))\(_2\)), manganese (II) acetate (Mn(COOCH\(_3\))\(_2\)), cobalt (II) acetate tetrahydrate (Co(COOCH\(_3\))\(_2\)\(\cdot\)4H\(_2\)O), nickel (II) acetate tetrahydrate (Ni(COOCH\(_3\))\(_2\)\(\cdot\)4H\(_2\)O), N,N-dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), thionyl (SOCl\(_2\)), and lithium ribbon were purchased from Sigma-Aldrich Co. LLC (USA). Aluminum foil was purchased from Pactogo Inc. (USA). Multi-walled carbon nanotubes (CNTs, purity of 95 wt\%) were purchased from Nanostructured & Amorphous Materials, Inc. (USA). Graphene flakes (flake thickness = 8 nm and average particle size = 550 nm) was purchased from Graphene Supermarket (USA). Triton X–100 was purchased from EMD Chemicals (USA). Lithium hexafluorophosphate (LiPF\(_6\)), ethylene carbonate (EC), and ethyl methyl carbonate (EMC) were purchased from Ferro Corporation (USA). Polyvinylidene fluoride (PVDF, 1,300,000 g mol\(^{-1}\)) was purchased from Thermo Fisher Scientific Inc. (USA). Commercial lithium iron phosphate (LiFePO\(_4\)) powder was purchased from Hydro-Quebec Inc. (Canada). The separators (Celgard 2400 and Celgard 480) were purchased from Celgard LLC (USA). Polytetrafluoroethylene (PTFE, 25 mm in diameter, 0.2 \(\mu\)m pores) filter was purchased from Millipore (USA). Cases, spring, gasket, spacer and commercial electrolyte (1M LiPF\(_6\) in a
mixture (1:1:1 by volume) of ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC)) were purchased from MTI Co. (USA).

3.2. Nanofiber preparation

Electrospun LiFePO$_4$/C, LiFePO$_4$/CNT/C and LiFePO$_4$/graphene/C composite nanofibers were prepared as cathode materials for lithium-ion batteries. Spinning solutions consisted of LiFePO$_4$ precursors, PAN, graphene flakes, and functionalized CNTs in DMF were prepared at room temperature by stirring for 24 h. For LiFePO$_4$ precursor, LiCO$_3$CH$_3$, H$_3$PO$_4$ and Fe(COOCH$_3$)$_2$ were mixed in DMF at a stoichiometric ratio of 1:1:1 by stirring at room temperature for 24 h. Functionalized CNTs were dispersed in DMF. Separately prepared graphene, CNT, PAN and LiFePO$_4$ precursor solutions were then mixed with different ratios. Electrospinning solutions were loaded in a 10 mL plastic syringe fitted with a needle tip (inner diameter = 0.012 inch). A variable high voltage power supply (Gamma ES40P–20W/DAM) was used to provide a high voltage (around 14 kV) for electrospinning with 0.5 ml h$^{-1}$ flow rate and 15 cm needle-to-collector distance.

Thermal-treatments of composite nanofibers were done in an atmosphere-controlled furnace (Lucifer Inc., USA). The electrospun composite nanofibers were first stabilized in air environment between 200-280 °C for 5 h (heating rate was 5 °C min$^{-1}$) and then
calcinated/carbonized between 600-800 °C for different times in argon atmosphere (heating rate was 2 °C min⁻¹).

3.3. Nanopowder preparation

To produce LiFePO₄ powder, stoichiometric amounts of lithium acetate, iron (II) acetate, and phosphoric acid were dispersed in DMF to obtain 20 wt% concentration and mixed for 24 hours. After mixing, samples were dried at 80 °C for 6 hours and then calcined at 700 °C for 18 hours under argon.

To obtain xLi₂MnO₃·(1-x)LiCo₁/3Ni₁/3Mn₁/3O₂ composite nanopowders, lithium acetate, manganese (II) acetate, nickel (II) acetate tetrahydrate, and cobalt (II) acetate tetrahydrate with different stoichiometric amounts were dissolved in deionized water to obtain 20 wt% concentration and mixed for 6 hours. After mixing, samples were dried at 120 °C for 6 hours and then calcined at 900 °C for 10 hours under air.

3.4. Morphological and structural characterization

The morphology and diameter of heat-treated electrospun nanofibers and pristine LiFePO₄ powder were evaluated by using field emission scanning electron microscope
(FESEM–JEOL 6400F SEM at 5kV). The images were acquired and average fiber diameters were obtained by measuring 250 electrospun nanofibers in each sample using the Revolution software provided by 4pi Analysis. The microstructure of composite nanofibers was also observed using transmission electron microscope (Hitachi HF2000 TEM at 200kV). Samples were ultrasonically treated in a solution of ethanol and then deposited on 200-mesh carbon-coated copper grids. The elemental distribution in composite nanofibers was confirmed with elemental dispersive spectroscopy (EDS, Oxford ISIS EDS system).

Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectra were collected from a FTIR spectrometer (Nicolet 560) in the wave number range of 4000 – 700 cm\(^{-1}\) at room temperature. At least 32 scans were conducted to achieve an adequate signal-to-noise ratio.

The structural characterization of LiFePO\(_4\)/C, LiFePO\(_4\)/CNT/C, LiFePO\(_4\)/graphene/C composite nanofibers, and pristine LiFePO\(_4\) powders was also carried out by wide-angle X-ray diffraction (WAXD, Philips X’Pert PRO MRD HR X-Ray Diffraction System, Cu K\(\alpha\), \(\lambda=1.5405 \text{ Å}\) and small-angle X-ray diffraction (SAXD, Rigaku Smartlab X–Ray Diffraction System, Cu K\(\alpha\), \(\lambda=1.5405 \text{ Å}\)) in a 2\(\theta\) range of 5 – 60\(^\circ\), with 2\(\theta\) step-scan intervals of 0.05\(^\circ\). The structural variations of carbonaceous material in the composite nanofibers were identified by Raman spectroscopy (Renishaw Raman Microscobe, 633 nm HeNe Laser). The carbon contents of composite nanofibers were determined by elemental analysis (Perkin Elmer 2400 Series II CHNS/O Elemental Analyzer).
3.5. Electrochemical characterization

CR2032–type coin cells (diameter = 20 mm and height = 3.2 mm) were fabricated using lithium metal as the counter electrode in an argon-filled glove box. Electrospun LiFePO$_4$/C, LiFePO$_4$/CNT/C, and LiFePO$_4$/graphene/C nanofibers were directly used as the working electrode after punching. For comparison, a mixture of 80 wt% LiFePO$_4$ powder, 10 wt% PVDF binder and 10 wt% carbon black was dispersed in NMP. The obtained slurry was casted on aluminum foil, dried in air at 70 °C for 24 h, and subsequently dried in vacuum at 120 °C for 24 h to form a regular LiFePO$_4$ electrode.

The working electrode and battery parts (cases, springs, discs, etc.) were dried under vacuum at 120 °C for 12 h before assembling. Separators were also dried under vacuum at 60 °C for 24 h. The electrolyte used consisted of 1 M solution of LiPF$_6$ in a mixture of EC-DMC-DEC (1:1:1 by volume). Separators were soaked in the electrolyte for 24 h prior to cell assembling. The charge and discharge characteristics of the cathodes were evaluated using Arbin automatic battery cycler at various current rates (0.05 – 2 C, 1 C = 170 mA g$^{-1}$) in the range of 2.5 – 4.2 V versus Li/Li$^+$. Electrochemical impedance spectra (EIS) and cyclic voltammetry (CV) curves were obtained by using Gamry reference 600 Potentiostat. All electrochemical experiments were conducted at room temperature and all capacity values were calculated based on the weight of active material LiFePO$_4$. 
CHAPTER 4. FABRICATION AND ELECTROCHEMICAL CHARACTERISTICS OF ELECTROSPUN LiFePO$_4$/CARBON COMPOSITE NANOFIBERS FOR LITHIUM-ION BATTERIES

Abstract

LiFePO$_4$/C composite nanofibers were synthesized by using a combination of electrospinning and sol–gel techniques. Polyacrylonitrile (PAN) was used as an electrospinning media and a carbon source. LiFePO$_4$ precursor materials and PAN were dissolved in $N,N$-dimethylformamide separately and they were mixed before electrospinning. LiFePO$_4$ precursor/PAN nanofibers were heat treated, during which LiFePO$_4$ precursor transformed to energy-storage LiFePO$_4$ material and PAN was converted to carbon. The surface morphology and microstructure of the obtained LiFePO$_4$/C composite nanofibers were characterized using scanning electron microscopy, transmission electron microscopy, and elemental dispersive spectroscopy. X-ray diffraction measurements were also carried out in order to determine the structure of LiFePO$_4$/C composite nanofibers. Electrochemical performance of LiFePO$_4$/carbon composite nanofibers was evaluated in coin-type cells. Carbon content and heat treatment conditions (such as stabilization temperature, calcination/carbonization temperature, calcination/carbonization time, etc.) were optimized in terms of electrochemical performance.
4.1. Introduction

Among various alternative cathode materials, lithium iron phosphate (LiFePO$_4$), which was discovered by Goodenough in 1997, is gaining significant attention because of its relatively low cost, high discharge potential (very flat voltage curve around 3.4 V versus Li/Li$^+$), large specific capacity (170 mAh g$^{-1}$), good thermal stability, excellent cycling performance, low toxicity, and safe nature. However, LiFePO$_4$ has low conductivity ($\sim 10^{-9}$ S cm$^{-1}$), which leads to high impedance and low rate capability for batteries using that material. In order to overcome this problem, different approaches can be used including doping LiFePO$_4$ with metal ions, coating with carbonaceous materials and reducing the particle size, etc. LiFePO$_4$ is typically prepared by both solid-state and solution-based methods, which have been reviewed elsewhere. In this chapter, a different and promising approach, i.e., electrospinning, was used to obtain LiFePO$_4$/C composite nanofibers that have high conductivity and excellent electrochemical performance. Electrospinning is an effective way of producing nanofibers from polymer solution by using an electrical force. Electrospun nanofibers have been investigated for use in lithium-ion battery applications including cathodes, separators, and anodes. In this chapter, the preparation, morphology, and electrochemical performance of electrospun LiFePO$_4$/C composite fiber cathodes for lithium-ion batteries were presented.
4.2. Experimental

4.2.1. Sample preparation

Electrospun LiFePO$_4$/C composite nanofibers were produced as cathode materials for lithium-ion batteries. Spinning solutions consisted of polyacrylonitrile (PAN, Pfaltz & Bauer Inc., 150,000 g mol$^{-1}$) and LiFePO$_4$ precursor. PAN was used as the carbon source because it has high dielectric constant, which is crucial for electrospinning, and is a good source for carbon nanofibers.\textsuperscript{17, 27, 28} PAN was first dissolved in $N,N$-dimethylformamide (DMF, Aldrich) at room temperature by stirring for 24 h. For LiFePO$_4$ precursor, lithium acetate (LiCOOCH$_3$, Aldrich), phosphoric acid (H$_3$PO$_4$, Aldrich) and iron (II) acetate (Fe(COOCH$_3$)$_2$, Aldrich) were used as the starting materials and mixed in DMF at a stoichiometric ratio of 1:1:1 by stirring at room temperature for 24 h. Separately prepared PAN and LiFePO$_4$ precursor solutions were then mixed with different ratios to obtain electrospinning solutions.

Table 4.1. Concentrations of PAN, LiFePO$_4$ precursor and solvent in electrospinning solutions.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>PAN (wt%)</th>
<th>LiFePO$_4$ Precursor (wt%)</th>
<th>Solvent (DMF) (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>4</td>
<td>4</td>
<td>92</td>
</tr>
<tr>
<td>S2</td>
<td>4</td>
<td>8</td>
<td>88</td>
</tr>
<tr>
<td>S3</td>
<td>4</td>
<td>12</td>
<td>84</td>
</tr>
</tbody>
</table>
Table 4.1 shows the concentrations of PAN, LiFePO$_4$ precursor and DMF in the obtained electrospinning solutions (S1, S2, and S3). The PAN concentration was determined by taking into consideration of the spinnability of LiFePO$_4$ precursor/PAN mixed solutions and the carbon content in the resultant LiFePO$_4$/C composite nanofibers. A schematic diagram of the overall experimental procedure is shown in Figure 4.1.

Figure 4.1. Schematic diagram of experimental procedure.
Electrospinning solutions were placed in 10 ml syringes with metal needles of 0.012 in. in diameter. A power supply (ES40P-20W/DAM) was used to provide a high voltage (15 kV). Needle-to-collector distance was set as 15 cm and electrospun nanofibers were collected on an aluminum foil. Electrospun LiFePO$_4$ precursor/PAN nanofibers were heat treated in two steps as shown in Figure 4.2a. In the first step, nanofibers were stabilized under air. The process started at room temperature and reached 200, 240 or 280 °C with an increment rate of 5 °C min$^{-1}$. That temperature was maintained for 5 h to complete the stabilization process, during which the cyano side groups of PAN form cyclic rings mainly by a dehydrogenation process (Figure 4.2b). In the second step, nanofibers were calcined and carbonized at 600, 700 or 800 °C for different times under argon atmosphere. During calcination/carbonization, LiFePO$_4$ precursor transformed to energy-storage LiFePO$_4$ material and PAN became electrically conducting carbon (Figure 4.2c).

The unique aspect of this process is that PAN was not only used as an electrospinning media for providing the spinnability of LiFePO$_4$ precursor/PAN composite nanofibers but also as a carbon source in order to increase the conductivity of LiFePO$_4$. Unlike in previous studies such as mixing or coating LiFePO$_4$ with a conducting material, here, conductive coating and LiFePO$_4$ formation take place at the same time during heat treatment, which ensures nano-scale carbon coating on the particle surface and maximizes LiFePO$_4$–carbon interface.
4.2.2. Structure characterization

The morphology and diameter of electrospun nanofibers and their heat-treated products were evaluated by using field emission scanning electron microscope (FESEM-JEOL 6400F SEM at 5 kV). The microstructure of heat-treated LiFePO$_4$/C composite nanofibers was observed using transmission electron microscope (Hitachi HF2000 TEM at 200 kV). TEM samples were ultrasonically treated in a solution of ethanol and then deposited on 200-mesh copper grids coated with carbon. The elemental distribution in LiFePO$_4$/C composite
nanofibers was confirmed with elemental dispersive spectroscopy (Oxford Isis EDS System). The structural characterization of LiFePO₄/C composite nanofibers was carried out by wide-angle X-ray diffraction (WAXD, Philips X’Pert PRO MRD HR X-Ray Diffraction System, Cu Kα, λ=1.5405 Å) in a 2θ range of 5 – 90°, with 2θ step-scan intervals of 0.05°. The carbon amounts of composite nanofibers were determined by elemental analysis (Perkin Elmer 2400 Series II CHNS/O Elemental Analyzer).

4.2.3. Electrochemical measurements

LiFePO₄/C composite nanofibers have a tap density of around 1 g cm⁻³ and they were directly used as the cathode without adding any polymer binder or conductive material. CR2032-type coin cells (diameter = 20 mm and height = 3.2 mm) were fabricated using lithium metal as a counter electrode in an argon-filled glove box. The cathode weight was around 2.5 mg per electrode. The electrolyte used consisted of a 1 M solution of LiPF₆ in a mixture (1:1 by volume) of ethylene carbonate (EC) and ethyl methyl carbonate (EMC). The separator (Celgard 2400) was soaked in the electrolyte for 24 h prior to testing. The charge and discharge characteristics of the cathode were evaluated at various current rates (0.05 – 2 C, 1 C = 170 mA g⁻¹) in the range of 2.5 – 4.2 V versus Li/Li⁺. All electrochemical experiments were conducted at room temperature and all capacity values were calculated based on the weight of active material LiFePO₄.
4.3. Results and discussion

4.3.1. Morphology of LiFePO$_4$ precursor/PAN and LiFePO$_4$/C composite nanofibers

Since the morphology and particle size of LiFePO$_4$ cathodes have great influence on their electrochemical performance, SEM analyses of electrospun LiFePO$_4$ precursor/PAN and heat-treated LiFePO$_4$/C composite nanofibers were carried out, and results are shown in Figures 4.3 and 4.4. The conditions used for heat-treating the nanofibers were: stabilization at 280 °C for 5 h and calcination/carbonization at 700 °C for 18 h. It is seen from Figure 4.3 that for all three samples, electrospun nanofibers form “network-like” structures. At the same time, variations in the fiber diameters are observed and beads are also formed. As shown in Figure 4.3d, with increase in LiFePO$_4$ precursor concentration, the average fiber diameter of electrospun LiFePO$_4$ precursor/PAN nanofibers decreases (i.e., $D_{S1} > D_{S2} > D_{S3}$). The diameter distributions of electrospun nanofibers were calculated using the following equation: \([D_{90} - D_{10}]/D_{50}\), where $D_{10}$, $D_{50}$, and $D_{90}$ are fiber diameters at which 10%, 50% and 90% of nanofibers are finer than, respectively. A lower distribution value indicates higher homogeneity. The distribution values of nanofibers electrospun from S1, S2, and S3 were calculated to be 1.7, 1.8, and 2.4, respectively, indicating that the nanofibers become less uniform when LiFePO$_4$ precursor concentration increases.
Heat treatment has influence on the morphology of electrospinning nanofibers. Comparing Figures 4.3 and 4.4, it is seen that after heat treatment, the fiber structure is still maintained; however, more beads are formed. In addition, substantial fiber diameter decrease is observed because of the removal of some species (such as CO$_2$, HCN, and NH$_3$, etc.) from the structure during heat treatment. Average diameter of heat-treated LiFePO$_4$/C nanofibers follows the same trend as electrospun nanofibers ($D_{S1} > D_{S2} > D_{S3}$). In addition, higher
LiFePO$_4$ precursor concentration leads to higher distribution value (i.e., 2.0, 2.2, and 3.2 for nanofibers prepared from S1, S2, and S3, respectively).

Figure 4.4. SEM images of LiFePO$_4$/C composite nanofibers prepared from (a) S1, (b) S2, and (c) S3, and (d) their diameter distributions.
The carbon contents of heat-treated LiFePO$_4$/C composite nanofibers were measured using elemental analysis and they are 22.5, 17.0, and 14.3 wt %, respectively, for nanofibers prepared from S1, S2, and S3.

Figure 4.5 shows a SEM image of LiFePO$_4$/C composite nanofibers (prepared from S2) and its corresponding EDS maps of phosphorous, iron, carbon, and oxygen (Li cannot be observed by EDS). Uniform element distribution of iron, phosphorous and oxygen throughout the sample can be seen clearly. In addition to SEM and EDS analyses, further evaluation was carried out by TEM in order to determine the particle microstructure and carbon coating characteristics.

Figure 4.6 shows TEM images of LiFePO$_4$/C composite nanofibers prepared from S1, S2, and S3. Nanofibers prepared from S2 and S3 showed relatively higher LiFePO$_4$ content compared with those from S1. This is consistent with the carbon content data measured by elemental analysis. LiFePO$_4$/C composite nanofibers prepared from S2 and S3 have lower carbon contents (17.0 and 14.3 wt %) and they have thinner carbon coatings of 8 and 12 nm, respectively (see magnified TEM images in Figure 4.6b and c). On the other hand, it is observed that nanofibers prepared from S1 have a carbon content of 22.5 wt % and show a carbon coating thickness of more than 15 nm (Figure 4.6a).
Figure 4.5 (a) SEM image and corresponding EDS maps of (b) phosphorus, (c) iron, (d) carbon, and (e) oxygen in LiFePO₄/C composite nanofibers prepared from S2.
4.3.2. Structure characteristics of LiFePO$_4$/C composite nanofibers

Figure 4.7a shows the XRD patterns of LiFePO$_4$/C composite nanofibers prepared from three electrospinning solutions (S1, S2, and S3). For comparison, the XRD pattern of pristine LiFePO$_4$ particles obtained by using the sol–gel method according to Ref. 242 is also shown in Figure 4.7a. The lattice parameters of all samples are the same to those given in the ICDD card (No. 96-110-1112). It is seen that all diffraction peaks of LiFePO$_4$/C composite nanofibers can be indexed to an olivine LiFePO$_4$ with orthorhombic crystal structure (Space Group: Pnma) and there are no impurity phase peaks. Therefore, the LiFePO$_4$ component in composite nanofibers is phase-pure. The presence of amorphous carbon contributes to the amorphous part in the diffraction pattern of LiFePO$_4$/C composite nanofibers.
Figure 4.7. X-Ray diffraction patterns of (a) LiFePO$_4$/C composite nanofibers obtained from S1, S2, S3 and pristine LiFePO$_4$, (b) LiFePO$_4$/C composite nanofibers obtained from S2 using different stabilization temperatures, (c) LiFePO$_4$/C composite nanofibers obtained from S2 using different calcination/carbonization temperatures, and (d) LiFePO$_4$/C composite nanofibers obtained from S2 using different calcination/carbonization times. The reflections of LiFePO$_4$ (ICDD No. 96-110-1112) are shown on all figures for comparison.
From Figure 4.7a, the average LiFePO$_4$ crystallite size, which is different than particle size, can be calculated by the Scherrer’s equation ($L = \frac{0.9\lambda}{\beta \cos \theta}$) from the full width at half maximum (FWHM or $\beta$) of (2 0 0), (1 0 1), (2 0 1) or (1 1 1), (0 2 0), and (3 1 1) peaks.$^{244}$ Crystallite sizes for LiFePO$_4$/C composite nanofibers prepared from S1, S2 and S3 were found to be 19, 21, and 22 nm, respectively.

Effects of heat-treatment conditions on the structure of LiFePO$_4$/C composite nanofibers prepared from S2 are shown in Figure 4.7b–d. Figure 4.7b shows the XRD patterns of LiFePO$_4$/C composite nanofibers prepared from S2 by using different stabilization temperatures (200, 240 and 280 °C). The calcination/carbonization temperature and time used were 700 °C and 18 h, respectively. It is seen that only low-intensity olivine peaks can be found for samples stabilized at 200 and 240 °C. When the stabilization temperature increases to 280 °C, the peaks become narrower and their intensities increase significantly, indicating increased crystallinity of LiFePO$_4$. Therefore, the appropriate stabilization temperature is 280 °C, which allows the formation of crystallized LiFePO$_4$ olivine phase. Figure 4.7c shows the XRD patterns of LiFePO$_4$/C composite nanofibers prepared from S2 using different calcination/carbonization temperatures (600, 700 and 800 °C for 18 h). The stabilization temperature used was 280 °C. It is seen that the diffraction peaks of all samples can be assigned to the olivine phase. In addition, the peaks become narrower with increase in calcination/carbonization temperature. The crystallite sizes were calculated to be 18, 21, to 28 nm, respectively, when the calcination/carbonization temperatures were 600, 700 and 800
°C. The XRD patterns of LiFePO$_4$/C composite nanofibers prepared from S2 using a calcination/carbonization temperature of 700 °C for 10, 12, 18 and 24 h are presented in Figure 4.7d. It is seen that all four fiber samples contain ordered olivine LiFePO$_4$ with orthorhombic Pnma structure. Crystallite sizes for LiFePO$_4$/C composite nanofibers obtained at 700 °C for 10, 12, 18 and 24 h were found to be 18, 19, 21 and 25 nm, respectively.

4.3.3. Electrochemical performance of LiFePO$_4$/C composite nanofibers

The first charge–discharge curves of LiFePO$_4$/C composite fiber cathodes prepared from three electrospinning solutions (S1, S2 and S3) are illustrated in Figure 4.8. The nanofibers were stabilized at 280 °C for 5 h and calcined/carbonized at 700 °C for 18 h. For nanofibers prepared from S2 and S3, flat voltage plateaus can be observed between 3.31–3.54 V and 3.26–3.55 V, which are the main characteristic of the two-phase reaction of LiFePO$_4$. However, nanofibers prepared from S1 show higher polarization and less flat plateaus between 2.96 and 3.87 V. This phenomenon is directly related to the carbon content in the composite.$^{245, 246}$ However, as shown in Figure 4.6a, higher amount of carbon content results in thicker carbon coating, which prevents penetration of the electrolyte to the active material and leads to higher polarization when the nanofibers were prepared from S1.

Figure 4.9 shows the cycling performances of LiFePO$_4$/C composite fiber cathodes prepared from three electrospinning solutions. It is seen that all three cathodes show good
cyclability. Instead of capacity fading, a slight increase in capacity can be observed after several cycles for all three cathodes, which may be attributed to slow electrolyte penetration into the electrode or the crack formation on the amorphous carbon layer during cycling that increases surface area of nanofibers and improves electrode–electrolyte interaction.\textsuperscript{236} From Figures 4.8 and 4.9, it is also seen that LiFePO\textsubscript{4}/C composite nanofibers prepared from S2 have higher capacities than those from S1 and S3. Therefore, S2 was used for additional experiments to further improve the electrochemical performance.

![Figure 4.8](image)

Figure 4.8. Initial charge - discharge curves of LiFePO\textsubscript{4}/C composite fiber cathodes prepared from S1, S2, and S3. Charge-discharge rate: 0.1C.
4.3.4. Effect of heat-treatment conditions

Stabilization temperature has great influence on the electrochemical performance of LiFePO$_4$/C composite nanofibers. Figure 4.10 shows the cycling performance of LiFePO$_4$/C composite nanofibers prepared from S2 using different stabilization temperatures. The stabilization time used was 5 h, and the calcination/carbonization temperature and time were 700 °C and 18 h, respectively. From Figure 4.10, it is seen that LiFePO$_4$/C composite nanofibers stabilized at 280 °C show discharge capacities of around 125 mAh g$^{-1}$ at 0.2 C. However, nanofibers stabilized at 200 and 240 °C for 5 h show no useful capacities. This phenomenon can be explained using the XRD data shown in Figure 4.7b. When the
stabilization temperature was 200 and 240 °C, no sufficient LiFePO₄ crystalline structure was formed, and hence the resultant LiFePO₄/C composite nanofibers have low capacities. In addition, stabilization temperatures of 200 and 240 °C are too low for stabilizing PAN to form cyclic rings, and as a result, no sufficient carbon is obtained in the resultant nanofibers. Therefore, the stabilization temperature selected for the following work was 280 °C. The electrochemical performance of LiFePO₄/C composite nanofibers is also directly affected by the calcination/carbonization temperature.

Figure 4.10. Effect of stabilization temperature on the discharge capacity of LiFePO₄/C composite nanofibers. Charge-discharge rate: 0.2C.
Figure 4.11 shows the cycling performance of LiFePO$_4$/C composite nanofibers stabilized at 280 °C for 5 h and calcined/carbonized at 600, 700 and 800 °C, respectively, for 18 h. It is seen that the average discharge capacities are 125, 141 and 136 mAh g$^{-1}$ at 0.1 C for 600, 700 and 800 °C. The best cycling performance is acquired from LiFePO$_4$/C composite nanofibers calcined/carbonized at 700 °C.

![Figure 4.11](image)

Figure 4.11. Effect of calcination/carbonization temperature on the discharge capacity of LiFePO$_4$/C composite nanofibers. Charge-discharge rate: 0.1C.

Calcination/carbonization time is another parameter that affects the electrochemical performance of LiFePO$_4$/C composite nanofibers. In order to investigate the effect of
calcination/carbonization time, nanofibers stabilized at 280 °C for 5 h were further calcined/carbonized at 700 °C for 10, 12, 18 and 24 h, respectively. As shown in Figure 4.12, when the calcination/carbonization time ranges between 10 and 18 h, the initial discharge capacity of LiFePO₄/C composite nanofibers increases with increase in calcination/carbonization time. However, with further increase in calcination/carbonization time after 18 h, the discharge capacity of LiFePO₄/C composite nanofibers decreases. As a result, LiFePO₄/C composite nanofibers calcined/carbonized at 700 °C for 18 h delivers the highest capacity of 166 mAh g⁻¹ at 0.05 C, which corresponds to 97% of the theoretical capacity.

Figure 4.12. Effect of calcination/carbonization time on the discharge capacity of LiFePO₄/C composite nanofibers. Charge-discharge rate: 0.05C.
Based on the results discussed above, it can be concluded that LiFePO$_4$/C composite nanofibers show the highest capacity and best cycling performance when they are prepared from S2 (8% LiFePO$_4$ precursor/4% PAN solution) by stabilizing at 280 °C for 5 h under air and calcinating/carbonizing at 700 °C for 18 h under argon.

Figure 4.13 shows the rate capability of these LiFePO$_4$/C composite nanofibers. During the test, the nanofibers were charged at 0.05 C, but discharged at different C-rates. Average discharge capacities are obtained as 162, 153, 136, 98, 71 and 37 mAh g$^{-1}$, respectively, for discharge rates of 0.05 C, 0.1 C, 0.2 C, 0.5 C, 1 C and 2 C. Although the rate capability
results are relatively good, they are still inadequate for certain applications, such as electrical vehicles (EVs) or hybrid electrical vehicles (HEVs). To overcome this problem, further work is required to increase the electronic and ionic conductivities of the composite nanofibers. For example, the ionic conductivity of the cathode is as important as the electronic conductivity, and hence research is needed to improve the ionic conductivity of LiFePO₄/C composite nanofibers. Work is also required to reduce the thickness and the amount of carbon in the electrodes to improve the kinetic at higher current densities. In addition, further work will also be focusing on establishing the processing–structure–performance relationships for these novel composite nanofibers and the use of such fundamental knowledge to achieve high-performance LiFePO₄/C composite nanofibers that can be used in next-generation lithium-ion batteries.

### 4.4. Summary

Electrospun LiFePO₄/C composite nanofibers with different carbon contents were synthesized and the synthesis conditions were investigated to improve the electrochemical performance. Homogeneously dispersed carbonaceous layer on LiFePO₄ and decreased particle size were achieved by electrospinning and subsequent heat-treatment. It was found that among all nanofibers studied, LiFePO₄/C composite nanofibers electrospun from 8% LiFePO₄ precursor/4% PAN solution, stabilized at 280 °C for 5 h under air, and then
calcined/carbonized at 700 °C for 18 h under argon, provided the best electrochemical performance. The results demonstrate that electrospinning is a promising approach to prepare high performance LiFePO₄/C composite nanofibers that have the potential to replace commercial cathodes for lithium-ion batteries.
CHAPTER 5. CARBON NANOTUBE-LOADED ELECTROSPUN LiFePO$_4$/CARBON COMPOSITE NANOFIBERS AS STABLE AND BINDER-FREE CATHODES FOR RECHARGEABLE LITHIUM-ION BATTERIES

Abstract

LiFePO$_4$/carbon nanotube (CNT)/C composite nanofibers were synthesized by using a combination of electrospinning and sol–gel techniques. Polyacrylonitrile (PAN) was used as the electrospinning media and carbon source. Functionalized CNTs were used to increase the conductivity of the composite. LiFePO$_4$ precursor materials, PAN and functionalized CNTs were dissolved or dispersed in $N,N$–dimethylformamide separately and they were mixed before electrospinning. LiFePO$_4$ precursor/CNT/PAN composite nanofibers were then heat-treated to obtain LiFePO$_4$/CNT/C composite nanofibers. Fourier transform infrared spectroscopy measurements were done to demonstrate the functionalization of CNTs. The structure of LiFePO$_4$/CNT/C composite nanofibers was determined by X–ray diffraction analysis. The surface morphology and microstructure of LiFePO$_4$/CNT/C composite nanofibers were characterized using scanning electron microscopy and transmission electron microscopy. Electrochemical performance of LiFePO$_4$/CNT/C composite nanofibers was evaluated in coin-type cells. Functionalized CNTs were found to be well-dispersed in the carbonaceous matrix and increased the electrochemical performance of the composite
nanofibers. As a result, cells using LiFePO$_4$/CNT/C composite nanofibers have good performance, in terms of large capacity, extended cycle life, and good rate capability.

5.1. Introduction

Rapidly increasing demand for lithium-ion batteries opened a new area in the cathode material research. Among various cathode materials, lithium iron phosphate (LiFePO$_4$) comes into prominence because of its high discharge potential, excellent cycling performance, good thermal stability, low toxicity, relatively low cost, and safe nature. However, LiFePO$_4$ has low conductivity (~$10^{-9}$ S cm$^{-1}$) which causes poor rate capability and high impedance.$^{232}$ In order to increase the efficiency of LiFePO$_4$, various structural and morphological modifications were proposed such as doping LiFePO$_4$ with metal ions,$^{232-234}$ reducing the particle size,$^{238, 251}$ coating with conductive materials,$^{235-237}$ and fabrication of conductive LiFePO$_4$ composites.$^{36, 95, 252-256}$ In all these methods, conductive LiFePO$_4$ composites are of increasing importance for their contribution to electrochemical performance. These materials are typically prepared by mixing LiFePO$_4$ or its precursors with a polymer, followed by a heat treatment procedure to convert the polymer matrix into a conductive carbon. The conductivity of these composites can be further improved by adding additional electrical conductors. Although many materials can be used to increase the electrical conductivity of the system,$^{256-258}$ carbon nanotubes (CNTs) are one of the most
promising materials due to their high electrical conductivity, large surface area, and high aspect ratio.$^{259, 260}$

LiFePO$_4$ is typically produced by both solid-state and solution-based methods, which have been reviewed elsewhere.$^{20, 50, 239, 261}$ In this chapter, LiFePO$_4$/CNT/C composite nanofibers were synthesized via the combination of electrospinning and sol-gel techniques and were used as binder-free cathodes for lithium-ion batteries. As schematically presented in Figure 5.1, CNTs can form conducting bridges between LiFePO$_4$ particles and increase the electrical conductivity of the system. In addition, the CNT-containing nanofiber structure restricts the particle agglomeration of LiFePO$_4$ during synthesis, and this further shortens the charge transfer distance and leads to increased lithium diffusion coefficient. Thus, LiFePO$_4$/CNT/C composite nanofibers not only have large capacity and good cycling performance, but also possess high rate capability. Here, we present the preparation, structure, morphology, and electrochemical performance of electrospun LiFePO$_4$/CNT/C composite nanofiber cathodes for lithium-ion batteries.
Figure 5.1. Schematic diagram of LiFePO$_4$/CNT/C composite nanofibers as cathodes for lithium-ion batteries.
5.2. Experimental

5.2.1. Functionalization of CNTs

Multi-walled CNTs with purity of 95 wt% were purchased from Nanostructured & Amorphous Materials, Inc. These CNTs are about 10–20 nm in diameter and 10–30 μm in length with an approximate surface area of 500 m² g⁻¹. As shown in Figure 5.2a, CNTs are found in entangled bundles caused by high level of van der Waals interactions between them. In addition, these CNTs have inert, stable structure because of the sp² hybridized carbon atoms. In order to increase the filler-matrix interaction and ensure good filler dispersion in the matrix, CNTs were chemically modified before use.

Figure 5.2. (a) SEM image of as-received CNTs, and (b) FT-IR spectra of unfunctionalized and functionalized CNTs.
Before the chemical modification, purification was carried out according to Ref. 253 in order to remove the catalyst. CNTs were treated with diluted sulfuric acid (50 wt%) at 140 °C for 3 h. Then, CNTs were filtered by using glass frit, washed with distilled water, and dried at 120 °C for 12 h. Purified CNTs were functionalized as described by Zhang et al.262 Firstly, 0.01 g of purified CNTs were oxidized in 100 ml of HNO₃ and H₂SO₄ mixture (1:3 by volume) solution by refluxing at 70 °C for 8 h and sonicated for 4 h to prepare carboxylic acid-functionalized CNTs (CNT-COOH). Then, the solution was filtered by vacuum filtration through a poly(tetrafluoroethylene) (PTFE) filter (Millipore, 25 mm in diameter, 0.2 μm pores) and washed with distilled water. In the next step, CNT–COOH mixture was treated with SOCl₂ (Fisher) at 65 °C for 24 h to obtain CNT–COCl, which was then mixed with Triton X–100 (EMD Chemicals) in N,N–dimethylformamide (DMF, Aldrich) and treated at 120 °C for 48 h. Under N₂ atmosphere, functionalized CNTs (i.e., CNT-Triton X) were filtered, washed with distilled water, and dried at room temperature for 24 h. Fourier transform infrared spectroscopy (FT–IR, Thermo Nicolet, Nexus 470) was used to demonstrate the functionalization of CNTs in ATR mode. The tests were carried out in the range between 700–4000 cm⁻¹ and FT-IR data were obtained by averaging 64 scans at a resolution of 4 cm⁻¹.
5.2.2. Preparation of composite nanofibers

Electrospun LiFePO$_4$/CNT/C composite nanofibers were prepared as cathode materials for lithium-ion batteries. Spinning solutions consisted of polyacrylonitrile (PAN, Pfaltz & Bauer Inc., 150,000 g mol$^{-1}$), functionalized CNTs, and LiFePO$_4$ precursor. PAN was used not only for the spinning media but also as the carbon source. PAN was first dissolved in DMF at room temperature by stirring for 24 h. For LiFePO$_4$ precursor, lithium acetate (LiCOOCH$_3$, Aldrich), phosphoric acid (H$_3$PO$_4$, Aldrich) and iron (II) acetate (Fe(COOCH$_3$)$_2$, Aldrich) were used as the starting materials and mixed in DMF at a stoichiometric ratio of 1:1:1 by stirring at room temperature for 24 h. Functionalized CNTs were dispersed in DMF. Separately prepared CNT, PAN and LiFePO$_4$ precursor solutions were then mixed and the concentrations of each component are given in Table 5.1.

Table 5.1. Concentrations of LiFePO$_4$ precursor, PAN, and CNT in electrospinning solutions.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>LiFePO$_4$ Precursor (wt%)</th>
<th>PAN (wt%)</th>
<th>Functionalized CNT (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiFePO$_4$ precursor/CNT/PAN</td>
<td>8</td>
<td>4</td>
<td>0.1</td>
</tr>
<tr>
<td>LiFePO$_4$ precursor/PAN</td>
<td>8</td>
<td>4</td>
<td>0</td>
</tr>
</tbody>
</table>
Electrospinning solutions were placed in 10 ml syringes with metal needles of 0.012 inch in diameter. A variable high voltage power supply (Gamma ES40P–20W/DAM) was used to provide a high voltage (around 14 kV) for electrospinning with 0.5 ml h\(^{-1}\) flow rate and 15 cm needle-to-collector distance. The electrospun LiFePO\(_4\) precursor/CNT/PAN composite nanofibers were first stabilized in air environment at 280 °C for 5 h (heating rate was 5 °C min\(^{-1}\)) and then calcinated/carbonized at 700 °C for 18 h in argon atmosphere (heating rate was 2 °C min\(^{-1}\)). Heat-treatment conditions were inclusively discussed in previous studies\(^{36}\).\(^{263}\) For comparison, electrospun LiFePO\(_4\)/C composite nanofibers were prepared without adding CNTs. Pristine LiFePO\(_4\) powder was also prepared by using the sol-gel method described in Ref. 242.

5.2.3. Structural and morphological characterization

The structural characterization of LiFePO\(_4\)/C and LiFePO\(_4\)/CNT/C composite nanofibers was carried out by small-angle X-ray diffraction (SAXD, Rigaku Smartlab X–Ray Diffraction System, Cu K\(_\alpha\), \(\lambda=1.5405\) Å) in a 2\(\theta\) range of 5 – 60°, with 2\(\theta\) step-scan intervals of 0.05°. The structural variations of carbonaceous material in the composite nanofibers were identified by Raman spectroscopy (Horiba Jobin Yvon LabRam Aramis Microscope, 633 nm HeNe Laser). The carbon contents of composite nanofibers were determined by elemental analysis (Perkin Elmer 2400 Series II CHNS/O Elemental Analyzer).
The morphology and diameter of heat-treated electrospun fibers and pristine LiFePO$_4$ powder were evaluated by using field emission scanning electron microscope (FESEM–JEOL 6400F SEM at 5kV). The microstructure of heat-treated LiFePO$_4$/CNT/C composite nanofibers was also observed using transmission electron microscope (Hitachi HF2000 TEM at 200kV). Before TEM observation, samples were ultrasonically treated in a solution of ethanol and then deposited on 200-mesh carbon-coated copper grids.

5.2.4. Electrochemical measurements

LiFePO$_4$/C and LiFePO$_4$/CNT/C composite nanofibers were directly used as the cathodes without adding any polymer binder or conductive material. For pristine LiFePO$_4$ powder, a mixture of 80 wt% active material, 10 wt% PVDF binder (Acros Organics, 1,300,000 g mol$^{-1}$) and 10 wt% carbon black was dispersed in N-methyl-2-pyrrolidone (Aldrich). The obtained slurry was casted on aluminum foil and dried in vacuum at 120 °C for 24 h. CR2032–type coin cells (diameter = 20 mm and height = 3.2 mm) were fabricated using lithium metal as the counter electrode in an argon-filled glove box. The cathode weight was around 2.5 mg per electrode. The electrolyte used consisted of 1 M solution of LiPF$_6$ in a mixture (1:1 by volume) of ethylene carbonate (EC) and diethyl carbonate (DEC). The separator (Celgard 480) was soaked in the electrolyte for 24 h prior to testing.
Electrochemical impedance spectrum (EIS) measurements were performed using a frequency response analyzer (Gamry Reference 600 Potentiostat) in a frequency range of 1 MHz to 0.001 Hz and a potentiostatic signal amplitude of 10 mV s$^{-1}$. The charge and discharge characteristics of the cathodes were evaluated at various current rates (0.05 – 2C, 1C = 170 mA g$^{-1}$) in the range of 2.5 – 4.2 V versus Li/Li$^+$. All electrochemical experiments were conducted at room temperature and all capacity values were calculated based on the weight of active material LiFePO$_4$.

5.3. Results and discussion

5.3.1. Structural and morphological characterization of pristine LiFePO$_4$ powder, and LiFePO$_4$/C and LiFePO$_4$/CNT/C composite nanofibers

Figure 5.2b shows the FT–IR spectra of purified CNTs and functionalized CNTs (i.e., CNT-Triton X). It is seen that in functionalized CNTs, new peaks occur at around 1240 and 1110 cm$^{-1}$, which indicate that Triton X has been successfully grafted onto the CNT surface. As previously reported,$^{262}$ these peaks were determined as C–O belonged to ester and C–O bonds occurred during the reaction between carboxylic acid and Triton X, respectively. In addition, new bands also appear around 1500 – 1600 cm$^{-1}$, which can be assigned to C=C bonding and attributed to the formation of electric dipoles caused by disruption of nanotube symmetry during surface modification.$^{264}$
Figure 5.3a shows the XRD patterns of pristine LiFePO$_4$ powder, LiFePO$_4$/C composite nanofibers, and LiFePO$_4$/CNT/C composite nanofibers produced at 700 °C for 18 h. The lattice parameters of all samples are the same to those given in the ICDD card (No. 96–110–1112). It is seen that all diffraction peaks of pristine LiFePO$_4$ powder, LiFePO$_4$/C composite nanofibers, and LiFePO$_4$/CNT/C composite nanofibers can be indexed to an olivine LiFePO$_4$ with orthorhombic crystal structure (Space Group: Pnma) and there are no impurity phase peaks. From Figure 5.3a, it is also seen that LiFePO$_4$/C and LiFePO$_4$/CNT/C composite nanofibers show broader olivine peaks with lower intensities, as compared with pristine LiFePO$_4$ powder. This is because the presence of carbon in the fiber structure slows down the crystal-growth during heat-treatment. From Figure 5.3a, the average LiFePO$_4$ crystallite size, which is different than particle size, can be calculated by the Scherrer's equation ($L = 0.9\lambda/\beta\cos\theta$) from the full width at half maximum (FWHM or $\beta$) of (2 0 0), (1 0 1), (2 0 1) or (1 1 1), (0 2 0), and (3 1 1) peaks. Crystallite sizes for pristine LiFePO$_4$ powder, and LiFePO$_4$/C and LiFePO$_4$/CNT/C composite nanofibers were calculated to be 45, 38, and 37 nm, respectively.

Figure 5.3b shows Raman spectra of LiFePO$_4$/C and LiFePO$_4$/CNT/C composite nanofibers. Both nanofibers show well-known D-band (disorder-induced phonon mode) in the range of 1250 - 1450 cm$^{-1}$ and G-band (graphite band) between 1550 and 1660 cm$^{-1}$. The peak at around 1350 cm$^{-1}$ is attributed to defects and disordered portions of carbon (sp$^3$-coordinated) and the peak at around 1600 cm$^{-1}$ is indicative of ordered graphitic crystallites.
of carbon (sp²-coordinated). The relative intensities (I_D/I_G) can be used to analyze the amount of carbon defects in the CNFs. Lower I_D/I_G ratio indicates the presence of larger amount of sp²-coordinated carbon.\textsuperscript{265-269} As shown in Table 5.2, I_D/I_G ratio decreases from 1.165 to 1.049 with the addition of CNTs in the precursor. Therefore, composite nanofibers without CNTs contain higher amount of disordered sections and defects. This also demonstrates that the presence of CNTs helps to create more ordered carbon in nanofibers.

Table 5.2. Characteristic Raman bands of LiFePO₄/C and LiFePO₄/CNT/C composite nanofibers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>D Peak (cm⁻¹)</th>
<th>G peak (cm⁻¹)</th>
<th>I_D/I_G value</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiFePO₄/C</td>
<td>1346</td>
<td>1579</td>
<td>1.165</td>
</tr>
<tr>
<td>LiFePO₄/CNT/C</td>
<td>1360</td>
<td>1589</td>
<td>1.049</td>
</tr>
</tbody>
</table>

SEM images and diameter distributions of the pristine LiFePO₄ powder, LiFePO₄/C composite nanofibers, and LiFePO₄/C composite nanofibers are shown in Figure 5.4, respectively. As shown in Figure 5.4a, pristine LiFePO₄ powder shows primary particle size in the range of 55 – 350 nm with an average of 197 nm. Although the primary particle size
seems to be low, it is apparent that they form agglomerates in the range of 1 – 175 µm with an average of 32 µm, which is an obstacle for electrolyte penetration. The size distribution of pristine LiFePO₄ powder is shown in Figure 5.4d.

Figure 5.3. (a) X-ray diffraction patterns and (b) Raman spectra of (i) pristine LiFePO₄ powder, (ii) LiFePO₄/C composite nanofibers, and (iii) LiFePO₄/CNT/C composite nanofibers. #: The reflections of LiFePO₄ (ICDD No. 96-110-1112) are shown for comparison.

As shown in Figures 5.4b and c, both LiFePO₄/C and LiFePO₄/CNT/C composite nanofibers kept their “network–like” structures after heat treatment. Comparing with Figure 5.4a, it can be found that the nanofiber structure restricts the agglomeration of LiFePO₄...
particles. During heat treatment, PAN matrix was converted to carbon, and at the same time, it prevented the formation of large aggregates of LiFePO$_4$ particles and ensured the homogeneous carbon coating on the surface of LiFePO$_4$ particles. From Figures 5.4e and f, slight differences in the fiber diameter and diameter distribution can be observed. While the average fiber diameter is 160 nm for LiFePO$_4$/C, it increases to 168 nm for LiFePO$_4$/CNT/C composite nanofibers. This may be caused by the increase in solution viscosity due to the addition of CNTs. Typically, higher solution viscosity results in larger fiber diameter due to the greater resistance of the solution to the stretching force caused by the charges in the electrospun jet.\textsuperscript{22, 23, 25, 36, 270}

Figure 5.5 represents TEM images of LiFePO$_4$/CNT/C composite nanofibers at different magnitudes. As shown in Figure 5.2b, CNTs have been successfully functionalized, which provides higher interaction with PAN matrix. The functionalization of CNTs leads to the separation of CNTs bundles and homogeneous dispersion throughout the composite.\textsuperscript{271, 272} LiFePO$_4$/CNT/C composite nanofibers consist of two types of conductors: carbon fiber matrix and CNTs. CNTs have higher electrical conductivity mainly due to their unique graphite wall structure.\textsuperscript{260} Well-dispersed CNTs can easily form a conducting network throughout the composite even at low concentrations because of their high aspect ratio.\textsuperscript{271, 272} As shown in Figure 5.5, functionalized CNTs form bridges between LiFePO$_4$ particles, which play an important role in enhancing the electron transport throughout the composite.\textsuperscript{273}
Figure 5.4. SEM images and diameter distributions of (a, d) pristine LiFePO$_4$ powder, (b, e) LiFePO$_4$/C composite nanofibers, and (c, f) LiFePO$_4$/CNT/C composite nanofibers.
From both SEM and TEM images, it is obvious that electrospinning is an effective way of minimizing the particle aggregation. During heat treatment, the transformation of PAN matrix to carbon leads to the formation of conductive layer on LiFePO$_4$ particles, increases the particle-to-particle distance, and prevents the particle aggregation. As shown in Figure 5.5c, the carbonaceous layer is as thin as 3 nm, which is beneficial for the penetration of Li ions.
5.3.2. Electrochemical performance of pristine LiFePO$_4$ powder, and LiFePO$_4$/C and LiFePO$_4$/CNT/C composite nanofibers

EIS measurements were carried out in the frequency range from 1 mHz to 1 MHz with an AC voltage signal of ±5 mV for pristine LiFePO$_4$ powder, LiFePO$_4$/C composite nanofibers, and LiFePO$_4$/CNT/C composite nanofibers. Prior to the EIS measurements, cells were firstly activated by five charge/discharge cycles at 0.05 C between 2.5 V and 4.2 V vs. Li/Li$^+$, and then they were polarized to 3.4 V. The potential was maintained for 5 h for the formation of a stable solid-electrolyte interface (SEI) film at the surface of the cathode.$^{257}$ Figure 5.6a illustrates the typical Nyquist plots of pristine LiFePO$_4$ powder, LiFePO$_4$/C composite nanofibers, and LiFePO$_4$/CNT/C composite nanofibers. The amplification of the high and medium frequency regions is also shown in Figure 5.6b. The intercept of the curve in high frequency to the real axis relates to the ohmic resistance of electrolyte ($R_O$). The depressed semicircle in medium frequency region is related to the charge transfer resistance ($R_{ct}$) at the particle surface. The increase in the semicircle radius indicates the increase in charge transfer resistance. The straight line in the low frequency region is related to the diffusion behavior of lithium ions within the LiFePO$_4$ particles or also called Warburg resistance ($Z_w$).$^{274-278}$

From Figure 5.6, charge transfer resistance ($R_{ct}$) values were calculated to be 7,360, 960.2 and 607.6 Ω, respectively, for pristine LiFePO$_4$ powder, LiFePO$_4$/C composite nanofibers, and LiFePO$_4$/CNT/C composite nanofibers. Among all samples, LiFePO$_4$/CNT/C composite nanofibers have the lowest $R_{ct}$ value, indicating that these nanofibers possess better reaction
kinetics of lithium ion insertion/extraction during electrochemical cycling than those of LiFePO₄/C composite nanofibers and pristine LiFePO₄ powder. The small charge transfer resistance of LiFePO₄/CNT/C composite nanofibers can be related to decreased particle size and relatively high carbon content.²⁷⁵,²⁷⁷

Figure 5.6. (a) Electrochemical impedance curves of pristine LiFePO₄ powder, LiFePO₄/C composite nanofibers, and LiFePO₄/CNT/C composite nanofibers, and (b) amplification of medium and high frequency regions.

Figure 5.7a shows the cycling performance of pristine LiFePO₄ powder, LiFePO₄/C composite nanofibers, and LiFePO₄/CNT/C composite nanofibers at a constant current density of 8.5 mA g⁻¹ (or 0.05 C). During the first three cycles, instead of capacity fading, a
slight increase in discharge capacity occurs for pristine LiFePO$_4$ powder and LiFePO$_4$/C composite nanofibers. This can be attributed to the slow electrolyte penetration into the electrodes or the crack formation on the amorphous carbon layer during cycling, which increases the electrode surface area and enhances the electrode-electrolyte interaction.$^{236}$ From Figure 5.7a, it is also seen that the reversible capacities remain relatively constant for LiFePO$_4$/C and LiFePO$_4$/CNT/C composite nanofibers (i.e., 161 and 169 mAh g$^{-1}$, respectively) over the entire fifty cycles. These values correspond to 95 and 99 % of the theoretical capacity of LiFePO$_4$. On the other hand, pristine LiFePO$_4$ powder shows a continuous capacity fading during fifty cycles. Reversible capacity of pristine LiFePO$_4$ powder decreases from 150 to 135 mAh g$^{-1}$, which corresponds to 90 % capacity retention from the first cycle.

Typical charge/discharge curves of pristine LiFePO$_4$ powder, LiFePO$_4$/C composite nanofibers, and LiFePO$_4$/CNT/C composite nanofibers are shown in Figure 5.7b. The charge/discharge curves were obtained at 0.05 C with a potential window of 2.5 – 4.2 V. It is seen that during the first cycle, LiFePO$_4$/C and LiFePO$_4$/CNT/C composite nanofibers show similar flat voltage plateaus at around 3.5 and 3.4 V, respectively, for charging and discharging, which are the characteristic behavior of the two-phase reaction of LiFePO$_4$. However, pristine LiFePO$_4$ powder shows higher polarization and its plateaus are at around 3.6 V (charging) and 3.3 V (discharging), respectively. From Figure 5.7b, it is also seen that initial reversible capacities are 150, 162 and 169 mAh g$^{-1}$, respectively, for pristine LiFePO$_4$
powder, LiFePO$_4$/C composite nanofibers and LiFePO$_4$/CNT/C composite nanofibers. The relatively good electrochemical performance of LiFePO$_4$/C and LiFePO$_4$/CNT/C composite nanofibers can be attributed to their unique one-dimensional fiber structure and the effective lithium-ion transportation on the large nanofiber surface.

Figure 5.7. (a) Cycling performance, (b) initial voltage vs. capacity curves, and (c) rate capabilities of pristine LiFePO$_4$ powder, LiFePO$_4$/C composite nanofibers, and LiFePO$_4$/CNT/C composite nanofibers. Charge–discharge rate used in (a, b) was 0.05 C.
Figure 5.7c shows the rate capabilities of pristine LiFePO$_4$ powder, LiFePO$_4$/C composite nanofibers, and LiFePO$_4$/CNT/C composite nanofibers. During the tests, the nanofibers were charged at 0.05 C, but discharged at different C-rates. When the C-rate increases from 0.05 to 2 C (i.e., from 8.5 to 340 mAh g$^{-1}$), LiFePO$_4$/CNT/C composite nanofibers show satisfactory rate capability compared with LiFePO$_4$/C composite nanofibers and pristine LiFePO$_4$ powder. It can be inferred that CNTs play a significant role in improving the reaction kinetics of LiFePO$_4$, especially, at high discharge rates, and this is also consistent with EIS measurements (Figure 5.6). Average reversible capacities of LiFePO$_4$/CNT/C composite nanofibers are obtained as 169, 165, 158, 148, 134, and 121 mAh g$^{-1}$, respectively, for discharge rates of 0.05 C, 0.1 C, 0.2 C, 0.5 C, 1 C, and 2 C.

The excellent electrochemical performance of LiFePO$_4$/CNT/C composite nanofibers is mainly caused by their unique structure. Carbon nanofiber matrix creates a conductive network-like structure throughout the electrode. The carbon nanofiber matrix also has high surface-to-volume ratio, complex porous structure, and shortened lithium-ion diffusion pathway, which enhance the electrode reaction kinetics and reduce the polarization. LiFePO$_4$ particles embedded in the carbon nanofiber matrix have small size, which is also beneficial for achieving higher reversible capacities. In addition, the incorporation of functionalized CNTs helps to form conducting bridges between particles and provides higher electrochemical efficiency. Therefore, LiFePO$_4$/CNT/C composite nanofibers have good cycling performance, high reversible capacity, and excellent rate capability.
5.4. Summary

Electrospun LiFePO$_4$/C and LiFePO$_4$/CNT/C composite nanofibers were synthesized using electrospinning, followed by heat treatment. Electrospinning was found as an effective way in minimizing the growth and aggregation of LiFePO$_4$ particles and promoting the formation of a conducting carbonaceous layer on LiFePO$_4$ particle surface. Functionalized CNTs were found to be well-dispersed in the matrix and help increase the electrochemical performance of the LiFePO$_4$ cathodes by forming conducting bridges between LiFePO$_4$ particles and increasing the electrical conductivity of the system.
CHAPTER 6. LiFePO$_4$ NANOPARTICLES ENCAPSULATED IN GRAPHENE-CONTAINING CARBON NANOFIBERS FOR USE AS ENERGY STORAGE MATERIALS

Abstract

LiFePO$_4$/graphene/C composite nanofibers, in which LiFePO$_4$ nanoparticles were encapsulated in graphene-containing carbon nanofiber matrix, were synthesized by using a combination of electrospinning and sol-gel techniques. Polyacrylonitrile (PAN) was used as the electrospinning media and the carbon source. Graphene was incorporated in order to increase the conductivity of the composite. PAN was dissolved in $N,N$–dimethylformamide (DMF). LiFePO$_4$ precursor and graphene were dispersed in DMF separately and were mixed with PAN solution before electrospinning. Electrospun fibers were heat-treated to obtain LiFePO$_4$/graphene/C composite nanofibers. The structure of LiFePO$_4$/graphene/C composite nanofibers was determined by X–ray diffraction analysis. The surface morphology and microstructure of LiFePO$_4$/graphene/C composite nanofibers were characterized using scanning electron microscopy and transmission electron microscopy. Electrochemical performance of LiFePO$_4$/graphene/C composite nanofibers was evaluated in coin-type cells. Graphene flakes were found to be well-dispersed in the carbonaceous matrix and increased the electrochemical performance of the composite nanofibers. As a result, cells containing
LiFePO$_4$/graphene/C composite nanofiber cathodes showed good electrochemical performance, in terms of capacity, cycle life, and rate capability.

6.1. Introduction

Recently, lithium iron phosphate (LiFePO$_4$) has become an alternative cathode material because of its high discharge potential, good thermal stability, excellent cycling performance, low toxicity, relatively low cost, and safe nature. However, LiFePO$_4$ shows low electrical conductivity (~$10^{-9}$ S cm$^{-1}$) which leads to poor rate capability and high impedance.$^{68,231,232}$ Different approaches were proposed in order to improve the electrochemical performance of LiFePO$_4$. Most of these methods aim to decrease the particle size and increase the electrical conductivity of LiFePO$_4$ by structural or morphological modifications including mechanochemical activation,$^{279}$ coating with conducting fillers,$^{235-237}$ and metal ion doping.$^{232-234}$

We recently proposed an alternative approach for fabrication of conducting LiFePO$_4$/C composite fibers through a combination of electrospinning and sol–gel techniques.$^{36}$ This approach basically consists of electrospinning of LiFePO$_4$ precursors/polymer solutions and heat-treatment of electrospun precursors to form electrically-conducting LiFePO$_4$/carbon cathode nanofibers. These conducting nanofibers have high surface-to-volume ratio, which is significant in terms of shortening lithium-ion diffusion pathway and increasing electrochemical performance of the system. In addition, carbon matrix is created \textit{in-situ}
during the formation of LiFePO₄, which restricts the growth and aggregation of LiFePO₄ particles, shortens the charge transfer distance, and leads to increased lithium diffusion coefficient. However, their rate capability is still unsatisfactory due to the limited conductivity of the carbon nanofiber matrix. Various conducting materials can be used in order to increase the conductivity of the system, including carbon nanotubes, graphite, carbon nanofibers, and graphene.

In this chapter, LiFePO₄/graphene/C composite nanofibers, in which LiFePO₄ nanoparticles were encapsulated in graphene-containing carbon nanofiber matrix, were prepared by introducing graphene into the electrospinning solution. Graphene, two-dimensional crystalline form of carbon, is a promising conductive material for many applications because of its superior electrical properties caused by the high mobility of charge carriers. In addition, graphene’s unique morphological properties, such as low thickness and high surface area, allow graphene-containing composites to have high electrical conductivity at very low concentrations. As a result, LiFePO₄/graphene/C composite nanofibers can not only have large capacity and good cycling performance, but also possess high rate capability. Here, the preparation, structure, morphology, and electrochemical performance of electrospun LiFePO₄/graphene/C composite nanofiber cathodes for lithium-ion batteries are presented.
6.2. Experimental

6.2.1. Preparation of composite nanofibers

Electrospun LiFePO₄/graphene/C composite nanofibers were prepared as cathode materials for lithium-ion batteries. Spinning solutions consisted of polyacrylonitrile (PAN, Pfaltz & Bauer Inc., 150,000 g mol⁻¹), graphene flakes (Graphene Supermarket, average flake thickness = 8 nm and average particle size = 550 nm, and electrical conductivity = ~10⁵ S m⁻¹), and LiFePO₄ precursor. PAN was used not only as the spinning media, but also as the carbon source. PAN was first dissolved in N,N–dimethylformamide (DMF, Aldrich) at room temperature by stirring for 24 h. For LiFePO₄ precursor, lithium acetate (LiCOOCH₃, Aldrich), phosphoric acid (H₃PO₄, Aldrich) and iron (II) acetate (Fe(COOCH₃)₂, Aldrich) were used as the starting materials and mixed in DMF at a stoichiometric ratio of 1:1:1 by stirring at room temperature for 24 h. Graphene flakes were dispersed in DMF. Separately prepared graphene, PAN and LiFePO₄ precursor solutions were then mixed and the concentrations of each component are given in Table 6.1.

Electrospinning solutions were placed in 10 ml syringes with metal needles of 0.012 inch in diameter. A variable high voltage power supply (Gamma ES40P–20W/DAM) was used to provide a high voltage of around 14 kV for electrospinning with 0.5 ml h⁻¹ flow rate and 15 cm needle-to-collector distance. Electrospun LiFePO₄ precursor/graphene/PAN composite nanofibers were first stabilized in air environment at 280 °C for 5 h (heating rate was 5 °C
min\(^{-1}\) and then calcinated/carbonized at 700 °C for 18 h in argon atmosphere (heating rate was 2 °C min\(^{-1}\)). Heat-treatment conditions were inclusively discussed in previous studies.\(^{36}\) For comparison, LiFePO\(_4\)/C composite nanofibers were prepared without adding graphene flakes. Pristine LiFePO\(_4\) powder was also prepared by using the sol-gel method described in Ref. 190.

Table 6.1. Concentrations of LiFePO\(_4\) precursor, PAN, and graphene in electrospinning solutions.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>LiFePO(_4) Precursor (wt%)</th>
<th>PAN (wt%)</th>
<th>Graphene (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiFePO(_4) precursor/PAN</td>
<td>8</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>LiFePO(_4) precursor/graphene/PAN</td>
<td>8</td>
<td>4</td>
<td>0.1</td>
</tr>
</tbody>
</table>

6.2.2. Structural and morphological characterization

The structural characterization of LiFePO\(_4\)/C and LiFePO\(_4\)/graphene/C composite nanofibers was carried out by small-angle X-ray diffraction (SAXD, Rigaku Smartlab X-Ray Diffraction System, Cu K\(\alpha\), \(\lambda=1.5405\) Å) in a 2\(\theta\) range of 5 – 60°, with 2\(\theta\) step-scan intervals of 0.05°. The carbon contents of composite nanofibers were determined by elemental
analysis (Perkin Elmer 2400 Series II CHNS/O Elemental Analyzer). The morphology and diameter of heat-treated composite nanofibers and pristine LiFePO$_4$ powder were evaluated by using JEOL 6400F field emission scanning electron microscope (SEM) at 5 kV. The microstructure of heat-treated LiFePO$_4$/C and LiFePO$_4$/graphene/C composite nanofibers was also observed by using Hitachi HF2000 transmission electron microscope (TEM) at 200kV. Samples were ultrasonically treated in a solution of ethanol and then deposited on 200-mesh carbon-coated copper grids.

6.2.3. Cathode preparation

LiFePO$_4$/C and LiFePO$_4$/graphene/C composite nanofibers formed free-standing porous mats and they were directly used as the cathodes without adding any polymer binder or conductive material. For pristine LiFePO$_4$ powder, a mixture of 80 wt% active material, 10 wt% PVDF binder (Acros Organics, 1,300,000 g mol$^{-1}$) and 10 wt% carbon black was dispersed in N-methyl-2-pyrrolidone (Aldrich). The obtained slurry was casted on aluminum foil and dried in vacuum at 120 °C for 24 h. Samples were punched into circular disks of 0.95 cm$^2$. The cathode weight was around 2.5 mg per electrode.
6.2.4. Electrochemical measurements

CR2032–type coin cells (diameter = 20 mm and height = 3.2 mm) were fabricated using lithium metal as the counter electrode in an argon-filled glove box. The electrolyte used consisted of 1 M solution of LiPF$_6$ in a mixture (1:1:1 by volume) of ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC). The separator (Celgard 480) was soaked in the electrolyte for 24 h prior to cell assembly. The charge and discharge characteristics of the cathodes were evaluated at various current rates (0.05 – 2 C, 1 C = 170 mA g$^{-1}$) in the range of 2.5 – 4.2 V versus Li/Li$^+$. All electrochemical experiments were conducted at room temperature and all capacity values were calculated based on the weight of active material LiFePO$_4$.

6.3. Results and discussion

6.3.1. Structure and morphology of pristine LiFePO$_4$ powder, LiFePO$_4$/C and LiFePO$_4$/graphene/C composite nanofibers

Figure 6.1 shows the X-ray diffraction (XRD) patterns of pristine LiFePO$_4$ powder, LiFePO$_4$/C composite nanofibers, and LiFePO$_4$/graphene/C composite nanofibers produced at 700 °C for 18 h. The lattice parameters of all samples are the same to those given in the ICDD card (No. 01–081–1173). It is seen that all diffraction peaks of pristine LiFePO$_4$
powder, LiFePO$_4$/C composite nanofibers, and LiFePO$_4$/graphene/C composite nanofibers can be indexed to an olivine LiFePO$_4$ with orthorhombic crystal structure (Space Group: Pnma) and there are no impurity phase peaks. In LiFePO$_4$/graphene/C composite nanofibers, a new peak is observed around $2\theta = 26.5^\circ$, which can be attributed to a graphite-like structure (002). This is because of the incomplete exfoliation of graphite oxide during graphene sheet production.$^{290}$ In this study, graphene flakes were used as-received without further exfoliation. These flakes consist of 20-30 monolayers through thickness.

Figure 6.1. XRD patterns of (a) LiFePO$_4$/graphene/C composite nanofibers, (b) LiFePO$_4$/C composite nanofibers, and (c) pristine LiFePO$_4$ powder. (d) The reflections of LiFePO$_4$ (ICDD No. 01-081-1173) are shown for comparison.
The lattice parameters and unit cell volumes of pristine LiFePO$_4$ powder, LiFePO$_4$/C composite nanofibers, and LiFePO$_4$/graphene/C composite nanofibers are given in Table 6.2. Compared with pristine LiFePO$_4$ powder, LiFePO$_4$/C and LiFePO$_4$/graphene/C composite nanofibers have comparable lattice constants and unit cell volumes. This indicates that the presence of carbon in the fiber structure does not have apparent effect on the growth of LiFePO$_4$ crystals during the heat-treatment step. The carbon contents of heat-treated products were measured by using elemental analysis and they were found to be 0.75, 22.8 and 24.2 wt. %, respectively, for pristine LiFePO$_4$ powder, LiFePO$_4$/C composite nanofibers, and LiFePO$_4$/graphene/C composite nanofibers.

Table 6.2. Structural lattice parameters and unit cell volumes of pristine LiFePO$_4$ powder, LiFePO$_4$/C composite nanofibers, and LiFePO$_4$/graphene/C composite nanofibers.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>V (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine LiFePO$_4$ powder</td>
<td>10.3067</td>
<td>6.0001</td>
<td>4.6955</td>
<td>290.37</td>
</tr>
<tr>
<td>LiFePO$_4$/C composite nanofibers</td>
<td>10.3052</td>
<td>5.9956</td>
<td>4.6938</td>
<td>290.01</td>
</tr>
<tr>
<td>LiFePO$_4$/graphene/C composite nanofibers</td>
<td>10.3047</td>
<td>5.9860</td>
<td>4.6897</td>
<td>289.27</td>
</tr>
</tbody>
</table>
Figure 6.2 shows Raman spectra of LiFePO$_4$/C and LiFePO$_4$/graphene/C composite nanofibers. Both nanofibers show well-known D-band (disorder-induced phonon mode) in the range of 1250 - 1450 cm$^{-1}$ and G-band (graphite band) between 1550 and 1660 cm$^{-1}$. The peak at around 1350 cm$^{-1}$ is attributed to defects and disordered portions of carbon (sp$^3$-coordinated) and the peak at around 1600 cm$^{-1}$ is indicative of ordered graphitic crystallites of carbon (sp$^2$-coordinated). The relative intensities ($I_D/I_G$) can be used to analyze the amount of carbon defects in the CNFs. Lower $I_D/I_G$ ratio indicates the presence of larger amount of sp$^2$-coordinated carbon.$^{265-269}$ As shown in Table 6.3, $I_D/I_G$ ratio decreases from 1.125 to 1.044 with the addition of graphene into the precursor. Therefore, composite nanofibers without graphene contain higher amount of disordered sections and defects. This also demonstrates that the presence of graphene helps to create more ordered carbon in nanofibers.

Figure 6.2. Raman spectra of (a) LiFePO$_4$/C, and (b) LiFePO$_4$/graphene/C composite nanofibers.
Table 6.3. Characteristic Raman bands of LiFePO$_4$/C and LiFePO$_4$/graphene/C composite nanofibers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>D Peak (cm$^{-1}$)</th>
<th>G peak (cm$^{-1}$)</th>
<th>$I_D/I_G$ Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiFePO$_4$/C</td>
<td>1338</td>
<td>1591</td>
<td>1.125</td>
</tr>
<tr>
<td>LiFePO$_4$/graphene/C</td>
<td>1358</td>
<td>1593</td>
<td>1.044</td>
</tr>
</tbody>
</table>

SEM images and diameter distributions of pristine LiFePO$_4$ powder, LiFePO$_4$/C composite nanofibers, and LiFePO$_4$/graphene/C composite nanofibers are shown in Figure 6.3, respectively. As shown in Figure 6.3a, pristine LiFePO$_4$ powder exhibits primary particle size in the range of 55 – 350 nm with an average of 197 nm. Although the primary particle size seems to be small, it is apparent that LiFePO$_4$ particles form agglomerates in the range of 1 – 175 µm with an average of 32 µm, which is an important obstacle for electrolyte penetration. The size distribution of pristine LiFePO$_4$ powder is also shown in Figure 6.3d.

As shown in Figures 6.3b and c, both LiFePO$_4$/C and LiFePO$_4$/graphene/C composite nanofibers kept their “network–like” structure after heat treatment, which is of significance for fast charge transfer throughout the system. Comparing with Figure 6.3a, it can be seen that the nanofiber structure restricted the growth and agglomeration of LiFePO$_4$ particles. During heat treatment, PAN matrix was converted into carbon and provided a carbon coating
on the surface of LiFePO$_4$ particles, and the presence of carbon prohibited the interaction between LiFePO$_4$ particles and the formation of large aggregates. In addition, graphene flakes with sharp edges can be observed in Figure 6.3c, as indicated with arrows in the inset. Graphene flakes are found to be homogeneously dispersed in composite nanofibers.

From Figures 6.3e and f, slight difference in the fiber diameter and diameter distribution can be observed between LiFePO$_4$/C and LiFePO$_4$/graphene/C composite nanofibers. The average fiber diameter is 160 nm for LiFePO$_4$/C composite nanofibers, and it increases to 163 nm for LiFePO$_4$/graphene/C composite nanofibers. This can be attributed to the increased viscosity of the electrospinning solution due to the addition of graphene. Typically, higher solution viscosity leads to larger fiber diameter.$^{270}$ Figure 6.4 compares the TEM images of LiFePO$_4$/C and LiFePO$_4$/graphene/C composite nanofibers. As shown in Figures 6.3a and b, LiFePO$_4$ particles are coated and connected with carbon to form LiFePO$_4$/C composite nanofibers. Similar morphology is observed for LiFePO$_4$/graphene/C composite nanofibers (Figures 6.4c and d). The only difference is that, in LiFePO$_4$/graphene/C composite nanofibers, graphene was successfully dispersed in the carbon matrix. By the incorporation of graphene, extra conductive bridges are formed between LiFePO$_4$ particles and throughout the composite nanofibers. Since graphene flakes have large surface area and low thickness, they play a significant role in increasing the electrical conductivity of the composite even at very low concentrations.$^{287, 293}$
Figure 6.3. SEM images and diameter distributions of (a, d) pristine LiFePO$_4$ powder (b, e) LiFePO$_4$/C composite nanofibers and (c, f) LiFePO$_4$/graphene/C composite nanofibers.
From both SEM and TEM images, it is obvious that the electrospinning approach is effective not only in coating LiFePO$_4$ particles, but also in minimizing their growth and aggregation. This is beneficial in increasing the reaction kinetics of the cathode material. In addition, the homogeneous dispersion of graphene in the matrix can increase the electronic conductivity of composite nanofibers due to the bridging effect.$^{294}$ The highly porous
structure of composite nanofibers can also allow the easy penetration of liquid electrolytes and enhance the electrode-electrolyte interactions during charging and discharging.\textsuperscript{236, 295}

6.3.2. Electrochemical performance of pristine LiFePO\textsubscript{4} powder, LiFePO\textsubscript{4}/C and LiFePO\textsubscript{4}/graphene/C composite nanofibers

Typical charge/discharge curves of pristine LiFePO\textsubscript{4} powder, LiFePO\textsubscript{4}/C composite nanofibers, and LiFePO\textsubscript{4}/graphene/C composite nanofibers are shown in Figure 6.5. The charge/discharge curves were obtained at 0.05 C with a potential window of 2.5 – 4.2 V. The LiFePO\textsubscript{4}/C and LiFePO\textsubscript{4}/graphene/C composite nanofibers exhibit very good reversibility of Li-ion during intercalation-deintercalation process. It is seen that during the first cycle, LiFePO\textsubscript{4}/C and LiFePO\textsubscript{4}/graphene/C composite nanofibers show similar flat voltage plateaus at around 3.5 and 3.4 V, respectively, for charging and discharging, which are the characteristic behavior of the two-phase reaction of LiFePO\textsubscript{4}. However, pristine LiFePO\textsubscript{4} powder shows higher polarization and its plateaus are at around 3.6 V (charging) and 3.3 V (discharging), respectively. For pristine LiFePO\textsubscript{4} powder, these anodic and cathodic reaction plateau values are parallel with the values reported by Iltchev \textit{et al.}\textsuperscript{190}
Figure 6.5. Initial voltage vs. capacity curves of pristine LiFePO$_4$ powder, LiFePO$_4$/C composite nanofibers, and LiFePO$_4$/graphene/C composite nanofibers. Charge–discharge rate: 0.05 C.

From Figure 6.5, it is also seen that initial reversible capacities are 150, 162 and 165 mAh g$^{-1}$, respectively, for pristine LiFePO$_4$ powder, LiFePO$_4$/C composite nanofibers, and LiFePO$_4$/graphene/C composite nanofibers. In this study, pristine LiFePO$_4$ powder synthesized by sol-gel method exhibits less electrical conductivity and also has larger particle size compared with LiFePO$_4$/C and LiFePO$_4$/graphene/C composite nanofibers. These maybe the major reasons of lower initial reversible capacity. The relatively good charge/discharge performance of LiFePO$_4$/C and LiFePO$_4$/graphene/C composite nanofibers can be attributed to their unique one-dimensional fiber structure and the effective lithium-ion transportation on the large nanofiber surface. In the case of LiFePO$_4$/C and LiFePO$_4$/graphene/C composite
Figure 6.6. Cycling performance of pristine LiFePO₄ powder, LiFePO₄/C composite nanofibers, and LiFePO₄/graphene/C composite nanofibers. Charge–discharge rate: 0.05 C.

Figure 6.6 shows the cycling performance of pristine LiFePO₄ powder, LiFePO₄/C composite nanofibers, and LiFePO₄/graphene/C composite nanofibers at 0.05 C. During the first five cycles, instead of capacity fading, a slight increase in discharge capacity occurs for pristine LiFePO₄ powder and LiFePO₄/C composite nanofibers. This can be attributed to the slow electrolyte penetration into the electrodes or the crack formation on the amorphous carbon layer during cycling, which increases the electrode surface area and enhances the

nanofibers, the nanofiber structure can provide a large surface area. This boosts the impregnation of electrolyte into the electrode, and improves the electrode/electrolyte interactions.
electrode-electrolyte interaction. After five cycles, pristine LiFePO$_4$ powder shows a continuous capacity fading during fifty cycles. Reversible capacity of pristine LiFePO$_4$ powder decreases from 150 to 135 mAh g$^{-1}$, which corresponds to 90 % capacity retention from the first cycle. On the other hand, the reversible capacities remain relatively constant for LiFePO$_4$/C and LiFePO$_4$/graphene/C composite nanofibers (i.e., 161 and 166 mAh g$^{-1}$, respectively). These values correspond to 95 and 97 % of the theoretical capacity of LiFePO$_4$. The lower capacity retention value of LiFePO$_4$ powder can be related with the chemical instability of pristine LiFePO$_4$ particles. Carbon coating can create a protection layer on particles and improve the chemical stability of LiFePO$_4$. 

Figure 6.7 shows the rate capabilities of pristine LiFePO$_4$, LiFePO$_4$/C composite nanofibers, and LiFePO$_4$/graphene/C composite nanofibers. During the test, the nanofibers were charged at 0.05 C, but discharged at different C-rates. When the C-rate increases from 0.05 to 2 C (i.e., from 8.5 to 340 mA g$^{-1}$), LiFePO$_4$/graphene/C composite nanofibers show satisfactory rate capability compared with LiFePO$_4$/C composite nanofibers and pristine LiFePO$_4$ powder. Average reversible capacities of LiFePO$_4$/graphene/C composite nanofibers are obtained as 163, 159, 153, 145, 132, and 107 mAh g$^{-1}$, respectively, for discharge rates of 0.05, 0.1, 0.2, 0.5, 1, and 2 C. It can be inferred that graphene plays a significant role in improving the reaction kinetics of LiFePO$_4$, especially, at high discharge rates. As seen from the results, incorporation of highly conductive and flexible graphene sheets into LiFePO$_4$/C composite nanofibers improves rate performance due to the increment
in electronic conductivity of composite.\textsuperscript{282} Also, the unique “network-like” nanofiber structure can provide continuous conducting pathways for Li\textsuperscript{+} and e\textsuperscript{-} transportation. These synergic effects help combine the virtues of both LiFePO\textsubscript{4}/C and LiFePO\textsubscript{4}/graphene/C composite nanofibers, and exhibit satisfactory overall electrochemical performance when used as cathodes in rechargeable lithium-ion batteries.

The excellent electrochemical performance of LiFePO\textsubscript{4}/graphene/C composite nanofibers is mainly caused by their unique structure. Carbon nanofiber matrix creates a conductive network-like structure throughout the electrode. The carbon nanofiber matrix also has high surface-to-volume ratio and shortened lithium-ion diffusion pathway, which enhance the electrode reaction kinetics and reduce the polarization. LiFePO\textsubscript{4} particles embedded in the carbon nanofiber matrix have small size, which is also beneficial for achieving higher reversible capacities. In addition, the incorporation of graphene flakes provides additional highly-conducting bridges between particles and provides greater electrochemical efficiency. Therefore, LiFePO\textsubscript{4}/graphene/C composite nanofibers have high reversible capacity, good cycling performance, and improved rate capability.
6.4. Summary

Electrospun LiFePO$_4$/C and LiFePO$_4$/graphene/C composite nanofibers were synthesized using electrospinning, following by heat treatment. Electrospinning was found as an effective way in order to minimize the growth and aggregation of LiFePO$_4$ particles, and promote the formation of a conducting carbonaceous layer on LiFePO$_4$ particle surface. Graphene flakes were found to be well-dispersed in the matrix of LiFePO$_4$/graphene/C composite nanofibers and help increase the electrochemical performance of the LiFePO$_4$ cathodes by forming conducting bridges between particles and increasing the electrical conductivity of the system.
CHAPTER 7. SYNTHESIS AND CHARACTERIZATION OF $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ COMPOSITE CATHODE MATERIALS FOR RECHARGEABLE LITHIUM-ION BATTERIES

Abstract

Various $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ($x = 0.1, 0.2, 0.3, 0.4,$ and $0.5$) cathode materials were prepared by the one-step sol-gel route. The structure of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ composites was determined by X-ray diffraction analysis. The surface morphology and microstructure of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ composites were characterized using scanning electron microscopy and transmission electron microscopy. Electrochemical performance of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ composites was evaluated in terms of capacity, cycling performance and rate capability. Although the morphology and structure were found to be affected by the $\text{Li}_2\text{MnO}_3$ content, all composites showed an $\alpha$-$\text{NaFeO}_2$ structure with $\text{R3m}$ space group. Electrochemical results showed that cells using $0.3\text{Li}_2\text{MnO}_3 \cdot 0.7\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ composites had good performance, in terms of large capacity, cycling stability, extended cycle life, and good rate capability.
7.1. Introduction

Li-ion batteries (LIBs) are being widely used for mobile electronics because of their high energy storage capacity and excellent rechargeability. LIBs became commercially available with the incorporation of lithium cobalt oxide (LiCoO$_2$) into the market by Sony in 1991. Although two decades pasted, LiCoO$_2$ is still the most used cathode material because of easy synthesis, relatively good cyclic stability and stable discharge voltage. On the other hand, LiCoO$_2$ is toxic, costly and has some safety issues. In addition, the energy density of LiCoO$_2$ is not sufficient for the electrical vehicle (EV) application since only half of its theoretical capacity can be achieved in practice due to the structural instability.$^{298-300}$

In order to minimize these problems, research efforts were initially focused on the substitution of LiCoO$_2$ with lithium manganese dioxide (LiMnO$_2$) and lithium nickel oxide (LiNiO$_2$) because of their lower cost, better safety and higher abundance in nature.$^{298-301}$ Although LiMnO$_2$ has the advantages of high safety and low cost, interaction of Mn with the electrolyte and poor cycling stability at high temperatures are major obstacles for its commercial use in lithium-ion batteries.$^{300}$ Likewise LiMnO$_2$, the use of LiNiO$_2$ in commercial lithium-ion batteries is also hindered due to its cyclic instability, thermal instability, and low safety.$^{300,302,303}$

Recently, by taking consideration of the advantages and disadvantages of the three abovementioned cathode materials, research focus has been shifted to mixed forms of layered
lithium metal (Li-Ni-Mn-Co) oxides. These new cathodes offer noticeable improvement in the capacity and cycling behavior. Among all Li-Ni-Mn-Co based cathode materials, LiNi_{1/3}Co_{1/3}Mn_{1/3}O_{2} attracted significant attention because of its good electrochemical properties such as high capacity, prolonged cycling life, and so on. However, this material still has drawbacks such as structural and thermal instabilities. To address this, researchers have recently developed layered Li-rich composite materials such as xLi_{2}MnO_{3}·(1-x)LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_{2}.

In xLi_{2}MnO_{3}·(1-x)LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_{2} composites, the Li_{2}MnO_{3} component can supply extra Li\textsuperscript{+} ions at voltages higher than 4.5 V (leading to increased operational voltage) and increase the structural and thermal stabilities. However, due to the composite-like structure, the electrochemical performance of xLi_{2}MnO_{3}·(1-x)LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_{2} is directly affected by the process and composition of the material. Therefore, it is critical to determine the optimum combination in a given material preparation route. In this study, we prepared xLi_{2}MnO_{3}·(1-x)LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_{2} (x=0.1, 0.2, 0.3, 0.4, 0.5) composite materials with different compositions by a one-step sol-gel route. The one-step method is simple and can be easily scaled up for industry production. Morphology, structure and electrochemical behavior of the prepared cathode materials were evaluated. Results show that with carefully controlled composition and structure, the prepared xLi_{2}MnO_{3}·(1-x)LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_{2} can present excellent electrochemical performance in terms of large capacity, good cycling stability, extended cycle life, and high rate capability. The good electrochemical performance together
with the low cost nature and simple preparation approach make it possible for using these new \( x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2 \) composite materials as promising cathode candidate in lithium-ion batteries.

Figure 7.1. Schematic diagram of preparation \( x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2 \) composite cathode materials for lithium-ion batteries.

7.2. Experimental

7.2.1. Preparation of cathode materials

Various cathode composite materials \( x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2 \) with different stoichiometric ratios \((x = 0.1, 0.2, 0.3, 0.4, \text{ and } 0.5)\) were prepared by a one-step sol–gel
method. Figure 7.1 shows the preparation procedure of \( x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2 \) composites. Precursors lithium acetate (LiCOOCH\(_3\), 99.99%, Sigma Aldrich), manganese (II) acetate (Mn(COOCH\(_3\))\(_2\), 98%, Sigma Aldrich), nickel (II) acetate tetrahydrate (Ni(COOCH\(_3\))\(_2\cdot4\)H\(_2\)O, 99.998%, Sigma Aldrich) and cobalt (II) acetate tetrahydrate (Co(COOCH\(_3\))\(_2\cdot4\)H\(_2\)O, 97%, Acros Organics) with different ratios were added in deionized water and were mixed for 6 hours. The total precursor concentration in all prepared solutions was fixed at 20 wt%. After mixing, samples were dried at 120 °C for 6 hours and then calcined at 900 °C for 10 hours. Table 7.1 shows the stoichiometric ratios of the acetate precursors used during the sample preparation and the theoretical capacities of the resultant \( x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2 \) composites.

**Table 7.1** Stoichiometric precursor ratios and the corresponding theoretical capacities of various \( x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2 \) composites.

<table>
<thead>
<tr>
<th>Chemical Formula</th>
<th>Li Acetate</th>
<th>Co Acetate</th>
<th>Ni Acetate</th>
<th>Mn Acetate</th>
<th>Theoretical Capacity (mAh g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 0.1\text{Li}<em>2\text{MnO}<em>3 \cdot 0.9\text{LiCo}</em>{1/3}\text{Ni}</em>{1/3}\text{Mn}_{1/3}\text{O}_2 )</td>
<td>1.1</td>
<td>0.30</td>
<td>0.30</td>
<td>0.40</td>
<td>299</td>
</tr>
<tr>
<td>( 0.2\text{Li}<em>2\text{MnO}<em>3 \cdot 0.8\text{LiCo}</em>{1/3}\text{Ni}</em>{1/3}\text{Mn}_{1/3}\text{O}_2 )</td>
<td>1.2</td>
<td>0.26</td>
<td>0.26</td>
<td>0.46</td>
<td>320</td>
</tr>
<tr>
<td>( 0.3\text{Li}<em>2\text{MnO}<em>3 \cdot 0.7\text{LiCo}</em>{1/3}\text{Ni}</em>{1/3}\text{Mn}_{1/3}\text{O}_2 )</td>
<td>1.3</td>
<td>0.23</td>
<td>0.23</td>
<td>0.53</td>
<td>340</td>
</tr>
<tr>
<td>( 0.4\text{Li}<em>2\text{MnO}<em>3 \cdot 0.6\text{LiCo}</em>{1/3}\text{Ni}</em>{1/3}\text{Mn}_{1/3}\text{O}_2 )</td>
<td>1.4</td>
<td>0.20</td>
<td>0.20</td>
<td>0.60</td>
<td>359</td>
</tr>
<tr>
<td>( 0.5\text{Li}<em>2\text{MnO}<em>3 \cdot 0.5\text{LiCo}</em>{1/3}\text{Ni}</em>{1/3}\text{Mn}_{1/3}\text{O}_2 )</td>
<td>1.5</td>
<td>0.16</td>
<td>0.16</td>
<td>0.66</td>
<td>377</td>
</tr>
</tbody>
</table>
7.2.2. Structural and morphological characterization

The structural characterization of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ composites was carried out by small-angle X-ray diffraction (SAXD, Rigaku Smartlab X−Ray Diffraction System, Cu Kα, $\lambda =1.5405$ Å) in a $2\theta$ range of $5 − 90^\circ$, with $2\theta$ step-scan intervals of 0.05°. The morphology and particle size distribution of the composites were evaluated by using field emission scanning electron microscope (FESEM−JEOL 6400F SEM at 5 kV). The microstructure was also observed using transmission electron microscope (Hitachi HF2000 TEM at 200 kV). Before TEM observation, composites were ultrasonically treated in a solution of ethanol and then deposited on 200-mesh carbon-coated copper grids.

7.2.3. Electrochemical measurements

Electrodes were prepared by mixing of 80 wt % active material, 10 wt % carbon black (Ketjen Black, Akzo Nobel), and 10 wt % poly(vinylene difluoride) (PVDF, 1,300,000 g mol$^{-1}$, Acros Organics) in 1-methyl-2-pyrrolidone (NMP, Aldrich). The obtained slurry was casted on aluminum foil and dried in a vacuum oven at 115 °C for 24 h. CR2032-type coin cells (diameter = 20 mm and height = 3.2 mm) were fabricated by using lithium metal as the counter electrode in an argon-filled glove box. The cathode weight was around 4 mg per electrode. The electrolyte used consisted of 1 M solution of LiPF$_6$ in a mixture (1:1:1 by volume) of ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate.
(DEC). The separator (Celgard 2400) was soaked in the electrolyte for 24 h prior to testing. Coin-cells were galvanostatically charged/discharged on Arbin BT2000 battery cycler at various current densities (where 1C = 299 mA g\(^{-1}\) for \(0.1\text{Li}_2\text{MnO}_3\cdot0.9\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2\), 1C = 320 mA g\(^{-1}\) for \(0.2\text{Li}_2\text{MnO}_3\cdot0.8\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2\), 1C = 340 mA g\(^{-1}\) for \(0.3\text{Li}_2\text{MnO}_3\cdot0.7\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2\), 1C = 359 mA g\(^{-1}\) for \(0.4\text{Li}_2\text{MnO}_3\cdot0.6\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2\), and 1C = 377 mA g\(^{-1}\) for \(0.5\text{Li}_2\text{MnO}_3\cdot0.5\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2\)).

7.3. Results and discussion

7.3.1. Structure of \(x\text{Li}_2\text{MnO}_3\cdot(1-x)\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2\) composites

The XRD patterns of \(x\text{Li}_2\text{MnO}_3\cdot(1-x)\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2\) \((x = 0.1, 0.2, 0.3, 0.4, \text{ and } 0.5)\) are shown in Figure 7.2. All five composites show a hexagonal α-NaFeO\(_2\) structure with R3\(_m\) space group, which is an indication of alternating layers of Li, Ni, Mn, Co in a single phase layered structure.\(^{312, 316, 321}\) Crystallite sizes of the composites were calculated by Scherrer’s equation and were found to be 102, 146, 187, and, and 204 nm for \(x\text{Li}_2\text{MnO}_3\cdot(1-x)\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2\) \((x = 0.1, 0.2, 0.3, 0.4, \text{ and } 0.5)\), respectively.

Magnified XRD patterns between 20° and 25° are given in Figure 7.2 inset (left). The peaks observed between 20° and 25° represent the existence of \(\text{Li}_2\text{MnO}_3\) phase in \(\text{LiMnO}_2\).\(^{312,\ldots}\)
The lattice parameters between 20° and 25° match with the ICDD card (No: 98-016-6861). The small peaks observed at 20.806° (020), 21.556° (110), 24.260° (111) also confirm the existence of monoclinic Li$_2$MnO$_3$ with C 2/m space group. In addition, the intensities of the peaks at 20.806° increase slightly while x increases from 0.1 to 0.5, which is an indication of increasing content and/or crystallinity of the Li$_2$MnO$_3$ phase in these composites.

Magnified XRD patterns between 63° and 67° are shown in Figure 7.2 inset (right). The intensity and separation of 64.622° (018) and 65.444° (110) peaks are the most noticeable in 0.3Li$_2$MnO$_3$·0.7LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$, which may reflect the higher structural order in this particular composite.

The intensity ratio of $I_{003}/I_{104}$ can be used for comparing the cation mixing degree of the layered structure among various composites. As reported previously, higher $I_{003}/I_{104}$ value indicates better structural order and a $I_{003}/I_{104}$ value of less than 1.2 reflects the undesirable cation mixing. The $I_{003}/I_{104}$ values for xLi$_2$MnO$_3$·(1-x)LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ (x = 0.1, 0.2, 0.3, 0.4 and 0.5) composites are 1.47, 1.53, 1.97, 1.66 and 1.47, respectively. The highest $I_{003}/I_{104}$ value is obtained for 0.3Li$_2$MnO$_3$·0.7LiMn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$O$_2$, indicating this composite has the highest structural order.

Another important parameter that is related to the order of the material structure is the $R$ factor which is defined as: $(I_{006}+I_{012})/I_{101}$. A lower R value represents better hexagonal order.
The $R$ values are 0.77, 0.69, 0.38, 0.53, and 0.76, respectively, for $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ($x = 0.1, 0.2, 0.3, 0.4$ and $0.5$) composites. Among all five composites, $0.3\text{Li}_2\text{MnO}_3 \cdot 0.7\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ gives the lowest $R$ value, indicating a better hexagonal order for this composite.$^{330,331}$

![X-ray diffraction patterns](image_url)

Figure 7.2. X-ray diffraction patterns of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ composites where (a) $x = 0.1$, (b) $x = 0.2$, (c) $x = 0.3$, (d) $x = 0.4$, and (e) $x = 0.5$. #: The reflections of LiMn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$O$_2$ (ICDD No. 98-016-2294) are shown for comparison.$^{326}$
These XRD results show that 0.3Li$_2$MnO$_3$·0.7LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ is the optimum composite for this route in terms of structural orders.

7.3.2. Morphology of xLi$_2$MnO$_3$·(1-x)LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ composites

Figure 7.3 shows the SEM images and particle size distributions of xLi$_2$MnO$_3$·(1-x)LiCo$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$ composites. Average particle sizes are determined to be 396, 457, 475, 485 and 699 nm, respectively, for xLi$_2$MnO$_3$·(1-x)LiCo$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$ (x = 0.1, 0.2, 0.3, 0.4, and 0.5). The gradual increase in particle size is probably caused by higher viscosity of the precursor solutions at higher x values. As shown in the magnified inset images, all composites are well-shaped with sharp edges and smooth surfaces. This can also be confirmed by the TEM image (Figure 7.4), which shows that 0.3Li$_2$MnO$_3$·0.7LiCo$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$ presents well-defined edges with a hexagonal layered structure.
Figure 7.3 SEM images and particle size distributions of \(x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2\) composites where (a, f) \(x = 0.1\), (b, g) \(x = 0.2\), (c, h) \(x = 0.3\), (d, i) \(x = 0.4\), and (e, j) \(x = 0.5\).
7.3.3. Electrochemical performance of $x\text{Li}_2\text{MnO}_3\cdot(1-x)\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ composites

Figure 7.5 shows the charge and discharge curves of $x\text{Li}_2\text{MnO}_3\cdot(1-x)\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ composites at a current density of 0.1C in a voltage range of 2 - 4.6 V. The Li$_2$MnO$_3$ content is critical in determining the electrochemical performance of the composites. The initial charge capacities are 136, 250, 292, 308, and 192 mAh g$^{-1}$, respectively, for $x\text{Li}_2\text{MnO}_3\cdot(1-x)\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ($x = 0.1, 0.2, 0.3, 0.4,$ and 0.5) composites. Initial discharge capacities are 63, 127, 184, 186, and 85 mAh g$^{-1}$, respectively. Among all five composites, $0.3\text{Li}_2\text{MnO}_3\cdot0.7\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and $0.4\text{Li}_2\text{MnO}_3\cdot0.6\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ show relatively high initial capacities.
Figure 7.5. Galvanostatic charge/discharge curves of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ composites where (a) $x = 0.1$, (b) $x = 0.2$, (c) $x = 0.3$, (d) $x = 0.4$, and (e) $x = 0.5$ at 0.1C.
From Figure 7.5, it is also seen that during charging, \(0.3\text{Li}_2\text{MnO}_3 \cdot 0.7\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2\) and \(0.4\text{Li}_2\text{MnO}_3 \cdot 0.6\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2\) show a wider plateau region between 3.75 to 4.0 V, as compared with other three composites.\(^{314,332}\) The electrode reaction between 3.75 and 4.0 V can be written as:

\[
\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2 \rightarrow \text{Li}_{1-y}\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2 + y e^- + y \text{Li}^+ 
\]  

(7.1)

Composites \(0.3\text{Li}_2\text{MnO}_3 \cdot 0.7\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2\) and \(0.4\text{Li}_2\text{MnO}_3 \cdot 0.6\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2\) also show a wider second plateau region at around 4.5 V, which can be attributed to the activation of inactive \(\text{Li}_2\text{MnO}_3\) content in the composite.\(^{314,332}\) The activation reaction at high potentials was previously given by Thackeray \textit{et al}.\(^{333}\) as:

\[
\text{Li}_2\text{MnO}_3 \rightarrow \text{MnO}_2 + \text{Li}_2\text{O} 
\]  

(7.2)

The \(0.1\text{Li}_2\text{MnO}_3 \cdot 0.9\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2\) composite does not show the second plateau probably because of the low \(\text{Li}_2\text{MnO}_3\) content\(^{314}\), confirmed by XRD data (see Figure 7.2). Although \(0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2\) has higher amount of \(\text{Li}_2\text{MnO}_3\) in the structure, the voltage used might not be high enough for the activation of this particular composite\(^{314,334}\) and a higher-voltage electrolyte might be required to discharge the composite to higher potentials to exhibit the second plateau region. From Figure 7.5, another important observation is the irreversible nature of the second plateau region after the first cycle. This was reported previously and attributed to the irreversible removal of Li and O from the structure during the activation of \(\text{Li}_2\text{MnO}_3\).\(^{318,334-337}\)
Figure 7.6. Cycling performances of $x\text{Li}_2\text{MnO}_3\cdot(1-x)\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ composites. (a) Discharge capacity, and (b) coulombic efficiency.

Figure 7.6 shows discharge capacities and corresponding coulombic efficiencies of $x\text{Li}_2\text{MnO}_3\cdot(1-x)\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ composites for 50 cycles. From Figure 7.6a, it is seen that at the 50th cycle, $x\text{Li}_2\text{MnO}_3\cdot(1-x)\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ($x = 0.1, 0.2, 0.3, 0.4,$ and 0.5)
composites show charge capacities of 51, 133, 184, 171, and 152 mAh g\(^{-1}\), respectively. In addition, except for 0.1Li\(_2\)MnO\(_3\)-0.9LiCo\(_{1/3}\)Ni\(_{1/3}\)Mn\(_{1/3}\)O\(_2\), the discharge capacities of the composites increase in the first few cycles, and then keep relatively constant. At the 50\(^{th}\) cycle, the capacity retentions are 79.3, 102.3, 89.7, 98.3, and 168%, respectively, for \(x\)Li\(_2\)MnO\(_3\)-(1-x)LiCo\(_{1/3}\)Ni\(_{1/3}\)Mn\(_{1/3}\)O\(_2\) (\(x = 0.1, 0.2, 0.3, 0.4, \text{ and } 0.5\)) composites. Among all five composites, 0.3Li\(_2\)MnO\(_3\)-0.7LiCo\(_{1/3}\)Ni\(_{1/3}\)Mn\(_{1/3}\)O\(_2\) shows the highest capacities in 50 cycles.

As given in Figure 7.6b, the first-cycle coulombic efficiencies are 46, 52, 65, 62, and 45%, respectively, for \(x\)Li\(_2\)MnO\(_3\)-(1-x)LiCo\(_{1/3}\)Ni\(_{1/3}\)Mn\(_{1/3}\)O\(_2\) (\(x = 0.1, 0.2, 0.3, 0.4, \text{ and } 0.5\)) composites. It is also obvious that all five composites show coulombic efficiencies greater than 95% after the first few cycles. From Figure 7.6, it can be concluded that among all five composites, 0.3Li\(_2\)MnO\(_3\)-0.7LiCo\(_{1/3}\)Ni\(_{1/3}\)Mn\(_{1/3}\)O\(_2\) shows the largest discharge capacity, highest initial coulombic efficiency, and best capacity retention at the 50\(^{th}\) cycle.

The rate capacity performance of 0.3Li\(_2\)MnO\(_3\)-0.7LiCo\(_{1/3}\)Ni\(_{1/3}\)Mn\(_{1/3}\)O\(_2\) was determined. Figure 7.7 shows the initial discharge curves of 0.3Li\(_2\)MnO\(_3\)-0.7LiCo\(_{1/3}\)Ni\(_{1/3}\)Mn\(_{1/3}\)O\(_2\) at various C-rates. It is seen that the discharge curves at different C-rates have the same shape. However, the plateau region is narrower at higher C-rates, which results in reduced discharge capacities. Discharge capacities of 0.3Li\(_2\)MnO\(_3\)-0.7LiCo\(_{1/3}\)Ni\(_{1/3}\)Mn\(_{1/3}\)O\(_2\) are determined to be 180, 170, 156, 130, 105, and 78 mAh g\(^{-1}\), respectively, under 0.1, 0.2, 0.5, 1C, 2C, and 4C. The decreased capacities at higher C-rates are caused by the high polarization of the material.
at high currents.\textsuperscript{314} Figure 7.8 shows the rate capabilities of

\[ 0.3 \text{Li}_2\text{MnO}_3 \cdot 0.7 \text{LiCo}_{\frac{1}{3}}\text{Ni}_{\frac{1}{3}}\text{Mn}_{\frac{1}{3}}\text{O}_2 \]

The composite shows good rate capability when the C-rate increases from 0.1 to 4 C. In addition, good cycling performance can observed at each C-rate for 5 cycles.

![Figure 7.7. Initial discharge curves of 0.3Li$_2$MnO$_3$·0.7LiMn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$O$_2$ under different C-rates.](image)

Figure 7.7. Initial discharge curves of 0.3Li$_2$MnO$_3$·0.7LiMn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$O$_2$ under different C-rates.
Based on the results discussed above, it can be concluded that among all five composites, 0.3Li$_2$MnO$_3$·0.7LiMn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$O$_2$ shows the highest capacity and best cycling performance. Although the rate capability results are relatively good, they are still inadequate for certain applications such as high-power electrical vehicles. This problem is related not only with the cathode structure, but also the electrolyte. To address this issue and enhance the cathode performance, further work is required for the determination of optimum electrolyte systems and the modification of the cathode structure and surface.
7.4. Summary

Various $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ($x = 0.1, 0.2, 0.3, 0.4,$ and $0.5$) cathode materials have been prepared by a one-step sol-gel route for use in lithium-ion batteries. The morphology, structure and electrochemical performance of the composites were found to be affected by the composite composition. Although all composites showed an $\alpha$-NaFeO$_2$ structure with R3m space group, the $0.3\text{Li}_2\text{MnO}_3 \cdot 0.7\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ composite presented the optimum structural order and the best electrochemical performance. The $0.3\text{Li}_2\text{MnO}_3 \cdot 0.7\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ composite showed discharge capacity of 184 mAh g$^{-1}$ at the first cycle and a capacity retention ratio of 98% at the 50$^{th}$ cycle with coulombic efficiencies ranging from 98 to 100% during cycling. Results demonstrated that the one-step sol-gel process is a promising approach to produce $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode materials with potentially high performance and low cost.
CHAPTER 8. CONCLUSIONS

To overcome worldwide critical energy demand and environmental pollution issues, development of sustainable, clean, and renewable energy technologies are of significant importance. Among various energy storage technologies, rechargeable lithium-ion batteries have been considered as effective solution to the increasing need for high-energy density electrochemical power sources. Rechargeable lithium-ion batteries offer energy densities 2-3 times and power densities 5-6 times higher than conventional Ni-Cd and Ni-MH batteries, and as a result, they weigh less and take less space for a given energy delivery. However, the use of lithium-ion batteries in many large applications such as electric vehicles and storage devices for future power grids is hindered by the poor thermal stability, relatively high toxicity, and high cost of lithium cobalt oxide (LiCoO$_2$) powders, which are currently used as the cathode material in commercial lithium-ion batteries. Recently, lithium iron phosphate (LiFePO$_4$) powders have become a favorable cathode material for lithium-ion batteries because of their low cost, high discharge potential (around 3.4 V versus Li/Li$^+$), large specific capacity (170 mAh g$^{-1}$), good thermal stability, and high abundance with the environmentally benign and safe nature. As a result, there is a huge demand for the production of high-performance LiFePO$_4$. However, LiFePO$_4$ also has its own limitation such as low conductivity ($\sim 10^{-9}$ S cm$^{-1}$), which results in poor rate capability. In order to obtain satisfied electrochemical performance and usage of LiFePO$_4$ for practical application
in lithium-ion batteries; small particle size, narrow size distribution, uniform morphology, optimum crystallinity degree, high specific surface area, minimum defects and agglomeration, and homogeneous carbon coating or metal doping are required. At that point, LiFePO$_4$/C nanofiber composites have become one of the promising nanostructured materials produced by combination of electrospinning and carbonization, and they can be potentially considered as efficient, simple, and inexpensive cathode materials. Electrospinning is an easy way of producing composites nanofibers with relatively low cost. The resultant composite nanofibers are promising materials for energy storage systems because of their large specific surface area, high aspect ratio, and unique structure.

Like LiFePO$_4$, $x$Li$_2$MnO$_3$·(1-$x$)LiCo$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$ composites are also promising materials for HEV or EV applications due to their low raw material cost, high theoretical capacities (more than 300 mAh g$^{-1}$), high working potentials (4.5-4.8 V vs. Li$^0$), consecutively high energy and power densities. The use of Li$_2$MnO$_3$ component in the composite can enhance the structural and thermal stability of LiCo$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$. However, due to the composite-like structure, the electrochemical performance of the $x$Li$_2$MnO$_3$·(1-$x$)LiCo$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$ composite is directly affected by the process and composition of the material. Therefore, it is also critical to determine the optimum combination in a given route.

This research was divided into the following four parts:
In Chapter 4, electrospun LiFePO$_4$/C composite fibers with different carbon contents were synthesized and the synthesis conditions were investigated to improve the electrochemical performance. Homogeneously dispersed carbonaceous layer on LiFePO$_4$ and decreased particle size were achieved by electrospinning and subsequent heat-treatment. It was found that among all fibers studied, LiFePO$_4$/C composite fibers electrospun from 8% LiFePO$_4$ precursor/4% PAN solution, stabilized at 280 °C for 5 h under air, and then calcined/carbonized at 700 °C for 18 h under argon, provided the best electrochemical performance. The results demonstrate that electrospinning is a promising approach to prepare high performance LiFePO$_4$/C composite fibers that have the potential to replace commercial cathodes for lithium-ion batteries.

In Chapter 5, electrospun LiFePO$_4$/CNT/C composite nanofibers were synthesized using electrospinning, followed by heat treatment. Electrospinning was found as an effective way in minimizing the aggregation of LiFePO$_4$ particles and promoting the formation of a conducting carbonaceous layer on LiFePO$_4$ particle surface. Functionalized CNTs were found to be well-dispersed in the matrix and help increase the electrochemical performance of the LiFePO$_4$ cathodes by forming conducting bridges between LiFePO$_4$ particles and increasing the electrical conductivity of the system.

In Chapter 6, electrospun LiFePO$_4$/graphene/C composite nanofibers were synthesized using electrospinning, following by heat treatment. Electrospinning was found as an effective way in order to minimize the aggregation of LiFePO$_4$ particles, and promote the formation of
a conducting carbonaceous layer on LiFePO$_4$ particle surface. Graphene flakes were found to be well-dispersed in the matrix of LiFePO$_4$/graphene/C composite nanofibers and help increase the electrochemical performance of the LiFePO$_4$ cathodes by forming conducting bridges between particles and increasing the electrical conductivity of the system.

In the Chapter 7, $x$Li$_2$MnO$_3$·(1-x)LiCo$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$ composite cathode materials with different Li$_2$MnO$_3$ contents were synthesized by a one-step sol-gel route. The morphology, structure and electrochemical performance of the composites were found to be affected by the composition of the cathode material. Our one-step sol-gel processing was found as an effective way to produce high performance $x$Li$_2$MnO$_3$·(1-x)LiCo$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$ composite cathode materials with low cost.
CHAPTER 9. RECOMMENDED FUTURE WORK

The recommended future work can include but not limited to:

I) As summarized in Chapters 4-6, electrochemical performance of the cathode is directly related with its conductivity. Fabrication of LiFePO₄/inherently conductive polymer (ICP) nanocomposites can be carried out in order to increase the conductivity of LiFePO₄ composites. Different ICPs can be used including polyaniline and polypyrrole. LiFePO₄/ICP composite nanofibers can be produced by the same route as explained in Chapter 4. By this method, LiFePO₄ powder will be incorporated into solution of an ICP and electrospun to form nanofiber cathodes. In order to obtain the optimum performance, the LiFePO₄/ICP ratio will be optimized.

II) Metal ion doping is another approach for increasing the intrinsic conductivity of LiFePO₄. Different metals can be used including lanthanum, rubidium, cobalt, nickel, manganese, etc. In the proposed future work, LiFePO₄ will be doped by a proper metal ion, and electrospinning and carbonization will be carried out as given in Chapters 4-6. Process will be optimized to achieve optimum carbon amount and electrochemical performance.

III) Our novel approach can be used for the fabrication of different cathode materials including LiCoₓNiᵧMn₂O₂, Li₂MSiO₄ compounds, etc. In Li₂MSiO₄ compounds, polyanion-containing frameworks can reversibly insert/extract two lithium ions per formula unit. This
would help to increase the capacity and energy density while benefiting from the highly stable covalently-bonded XO₄ groups. Process will be carried out in two approaches. In the first approach, compounds will be synthesized and incorporated into the PAN solution, electrospun and carbonized. In the second approach, precursor solutions will be mixed with PAN, electrospun and heat treated as discussed in Chapters 4-6.

IV) To improve the chemical, thermal and cyclic stability of xLi₂MnO₃·(1-x)LiCo₁/₃Ni₁/₃Mn₁/₃O₂ composites, various types of chemical and/or physical surface modification can be carried out. Amorphous metal oxides (i.e. Al₂O₃, ZnO, TiO₂) can be physically coated on cathode material or electrode by using plasma or atomic layer deposition. AlF₃, Al₂O₃, or other metal oxides or fluorides can be chemically coated on composite materials.

V) In addition to all these mentioned above, different core-shell structures can be fabricated by electrospinning, i.e. xLi₂MnO₃·(1-x)LiCo₁/₃Ni₁/₃Mn₁/₃O₂/TiO₂, xLi₂MnO₃·(1-x)LiCo₁/₃Ni₁/₃Mn₁/₃O₂/Al₂O₃, xLi₂MnO₃·(1-x)LiCo₁/₃Ni₁/₃Mn₁/₃O₂/ZnO, etc.
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