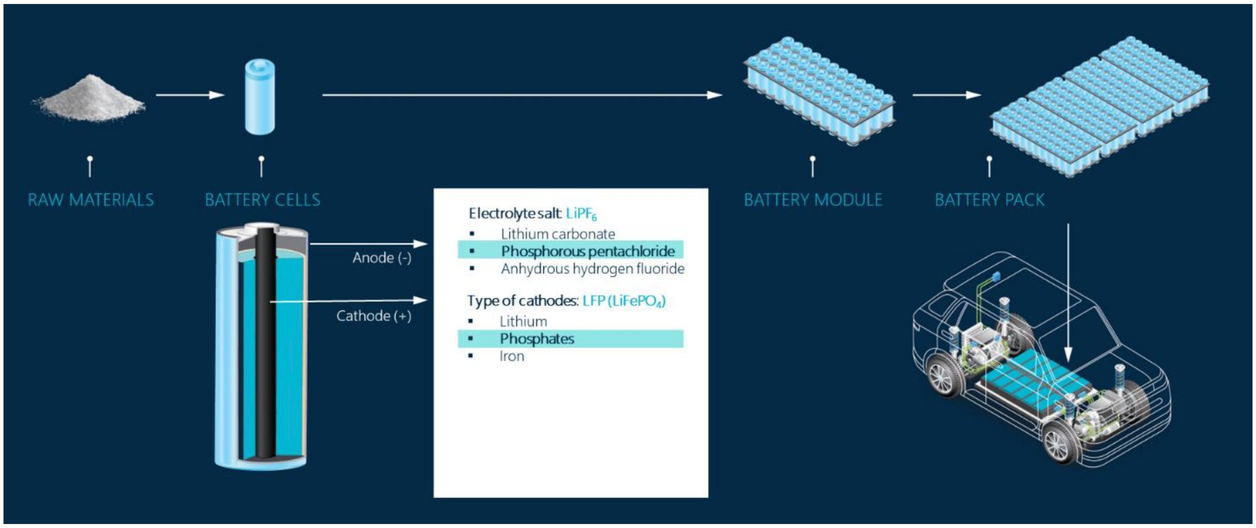
Lithium Iron Phosphate (LFP)

Lithium ion batteries (LIB) have a dominant position in both clean energy vehicles (EV) and energy storage systems (ESS), with significant penetration into both of the markets during recent years. However, supply chain and operational safety issues have plagued the manufacturers of the EV and ESS lately. Typical LIB cathode chemistries such as lithium cobalt oxide (LCO) and nickel manganese cobalt (NMC) chemistries are considered sensitive to operational abuse and create unsafe conditions, resulting in uncontrollable battery fires. LCO and NMC cathodes also contain significant amounts of cobalt, which is a critical mineral in low supply and often unethically mined. Lithium Iron Phosphate (LFP) cathode material contains only abundant elements - Iron and Phosphorous - besides Lithium and, although LIBs with LFP cathode have lower energy densities compared to LCO and NMC cathodes, they are free from cobalt and less likely to elicit operational abuse. LFP has the added value of excellent cycle life compared to other cathode materials. The benefits of LFP have resulted in several EV and ESS manufacturers announcing that a significant portion of their current and future products will have LFP batteries.



LFP cathode active material (CAM) can be prepared by both, solid state, and solution-based methods. Solid state techniques are carried out at high temperatures and, in general, are energy intensive and not practiced at commercial scale. On the other hand, solution-based methods consume relatively less energy and are based on reactions that take place in one of the following modes - (a) Hydrothermal Synthesis, (b) Spray Pyrolysis, (c) Sol-Gel Synthesis, and (d) Co-precipitation.

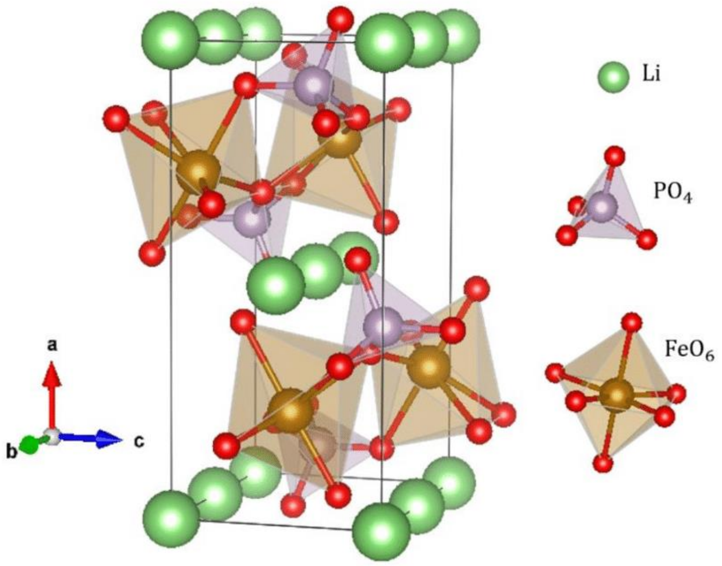
Sol-Gel Synthesis has low throughput and therefore is not ideal for high volume production. Co-precipitation requires fine control of process and solution parameters and therefore does not scale to very large production vessels, thus requiring large number of parallel processing tanks and spray pyrolysis is in its infancy – more research is required to scale it up to large production throughput. Commercial production follows the Hydrothermal Synthesis route, which requires relatively less energy. Several variations of this general method have been in practice for production of LFP.

Starting materials for LFP synthesis vary but are comprised of an iron source, lithium hydroxide or carbonate (an organic reducing agent), and a phosphate component. The iron raw material ranges from high purity elemental iron to low purity iron sulfate, which is a by-product of titanium dioxide production. Various iron oxides have also been successfully utilized in LFP synthesis along with specialty materials such as iron oxalate. The LFP CAM is generally free of metal impurities (<100 ppm) that can compromise battery life. This requires that one utilize a very pure iron source or incorporate a purification step into the process.

Lithium hydroxide and lithium carbonate are the two most common lithium sources available. The hydroxide is neutralized to produce water while the carbonate releases carbon dioxide and water in the presence of acid.

Many different organic materials can be used in the sintering of LFP precursor. Pyrolysis of organic materials has two effects. The first is the reduction of Fe^{+3} to Fe^{+2} needed to form the LFP olivine structure which is ionically conductive. The second is the critically important carbon coating formed upon pyrolysis to improve the electrical conductivity.

The bulk of LFP is comprised of a phosphate salt. Phosphate is roughly 70% by mass in LFP and can be utilized in a few different forms. The most common is a mixture of high purity phosphoric acid and battery grade monoammonium phosphate (MAP). This mixture allows one to control the pH during the iron (+3) phosphate synthesis via the iron sulfate route. Phosphoric acid is utilized when metallic iron powder is the iron source. Hydrogen generation is observed and must be controlled for safety reasons. Iron oxides can be used in combination with phosphoric acid or MAP as well.



Mixtures of the above materials in mole ratio of 1:1:1 of Li to Fe to Phosphate are sintered at temperatures of 600-750 C. Heating allows for the LFP precursor to rearrange to the olivine structure needed for ionic conductivity. The organic material present undergoes pyrolysis which deposits a carbon layer throughout the particle and on the surface to improve the electrical conductivity. A carbon layer of 1-3% is typically observed.

After sintering, the LFP material is jet milled to create a particle size distribution that maximizes packing density upon coating onto the aluminum cathode electrode with carbon black and PVDF binder.

The final quality control includes measurement and reporting of a wide range of parameters including Particle Size, BET Surface Area, and Electrochemical Capacity, Bulk Resistance, Carbon Content, and Moisture Content.

The future of phosphate materials in LIB does not stop with LFP. The next generation of materials currently under development is where a portion of the iron is replaced with manganese to achieve charge densities of similar parity to NMC materials. Scientists continue to optimize and refine the technology to improve the charge density and cycle life for applications and uses into the future.