

## Plasma-Driven Surface Engineering of LiFePO<sub>4</sub> Cathode and Implication for LIB Electrochemical Performance: A Mini Review

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### 1. Introduction

In order to realize the global vision of carbon net zero by 2050, scaled systems for electrification, and storage for power harnessed from renewables have become a practical alternative. Therefore, electrochemical energy devices, specifically Lithium-Ion Batteries (LIBs) are central in easing modern electrification, and other storage purposes. Notwithstanding, the performance of LIBs is largely dependent on properties of their electrode (cathode and anode) materials. Among other commercialized intercalation cathodes, LiFePO<sub>4</sub> (LFP) is recognized for its good structural, and cycling stability. However, it is limited by low electronic conductivity, and low Lithium-ion (Li<sup>+</sup>) diffusion rate.

The limitations are being addressed by using both solid state and wet chemistry approaches to modify the LFP material. Although they are effective, some of these methods are associated with high reaction temperatures (such as solvothermal), and others (e.g., precipitation) involve use of significant volumes of solvents, some of which may be toxic, and flammable. With the use of plasma irradiation technique (low temperature, and/or non-thermal) for material modification, the aforementioned setbacks associated with traditional approaches can be overcome.

Plasma is the fourth state of matter with a composition of ions, free radicals, electrons, and neutral particles. Plasma technique is viable for modifying LFP material through surface engineering, thus improving conductivity, and Li<sup>+</sup> transport [1]. This review therefore aims to briefly examine the recent progress made in plasma assisted modification of LFP material, and the impact on electrochemical performance. The review also discusses future prospects for broader application of plasma technology.

### 2. Methods and Results

#### 2.1 Plasma-induced modification mechanisms

Surface doping. Ionized species bombards the electrode material, in a vacuum environment. Depending on the energy, and the composition of plasma, these species can cause partial displacement, or substitution of pre-existing atoms in the material's lattice (surface). As a result, additional vacancies for energy storage may be created. Also, dopants can either introduce new energy levels, which reduce band gap for enhanced electron conductivity, or enable expansion of Li<sup>+</sup> pathways.

Surface coating. An electrically released plume of ionized gas forms a conformal layer onto the surface of the precursor [2]. In the case of conductive coatings like carbon, a continuous network of electrons is formed on the electrode particles. Such coatings act as a barrier from electrolyte attack, and side reactions, thus enhancing interfacial, and surface stability, as well as protection. Also, volume expansion is constrained by coating, which further enhances structural, and cycling stability.

Nanosizing via etching. Reactive plasma particles enable formation of secondary products with the electrode surface [1]. The products are subsequently removed, which generally reduces material's particle size. This increases the activation area, reduces electron tunneling barrier, and shortens the Li<sup>+</sup> diffusion length. Reduced length lowers resistance arising from solid state diffusion, and increases capability performance.

#### 2.2 Impact of plasma treatment on LiFePO<sub>4</sub> cathode, and LIB performance

Some studies have demonstrated that plasma irradiation modifies the LFP material properties, which eventually improves the LIB performance. In particular, plasma doping introduced Fluorine, and Nitrogen in the carbon coated LFP, which modified its electronic network [3]-[4]. Nitrogen doping uniquely enabled removal of antisite defects in the Lithium sites, which would otherwise hinder Li<sup>+</sup> diffusion. These alterations led to faster electron, and Lithium-ion transport kinetics, leading to improved rate capability (see table 1).

With regard to hybridized methods, a porous carbon coating on LFP was achieved via plasma assisted pyrolysis technique [5]. Such coating enhanced surface stability, and also enabled various channels for electron transfer. As a result, the cycling performance of LIB was superior. In another approach, when plasma was coupled with vapor deposition, nanosized active materials were synthesized with a thin carbon layer. Nanosizing ensured larger surface area, while coating reduced charge transfer resistance [6]. A summary of results on performance improvement due to plasma treatment are summarized in Table 1.

Table 1. Plasma modified LFP performance results

Modification approach	Initial discharge capacity (mAh/g)	Ref
Fluorine doping	130.1 vs 112.0 (bare) @ 2 C	[3]
Nitrogen doping	135.2 vs 80 (bare) @ 30 C	[4]
Porous carbon coating	166.9 @ 0.2 C	[5]
Nanosizing and coating	148.3 @ 5 C	[6]

### 2.3 Plasma technology challenges

Complex composition of plasma. As mentioned early, plasma includes ions, electrons, neutral particles, and free radicals. It is therefore difficult to selectively single out one species type of interest during the treatment process.

Cost consideration. While plasma is a promising technique, it involves a number of process controls, as well as vacuum maintenance, resulting into high operational costs. Hence, its deployment for large scale use may remain limited.

Limited plasma penetration depth. To a larger extent, low temperature plasma primarily performs surface treatment, disadvantaging in-depth ion implantation. In other instances, certain ionized gas chemistries may cause damage to the target material unintentionally.

### 2.4 Future prospects

Utilizing plasma technique for nano-metallic deposition. Beyond carbon coating, plasma can be used to decorate metallic particles (e.g., Zr, and Al) onto LFP material, creating additional electronic pathways for improved conductivity. Metallic coated LFP improves LIB performance without affecting its tap density. This will be useful for high power applications.

Modulating plasma conditions and parameters such as gas composition, power, and temperature. A balanced gradient between dopant composition, and defect engineering may result into deeper modification within the material's lattice. This can be beneficial for both high loading and thick electrodes.

## 3. Conclusions

In this review, recent efforts employing plasma for modifying LFP cathode material were examined. Plasma enables surface engineering via elemental doping, nanoscale coating, and etched-nanosizing. Although the number of studies is limited, available data reveals that plasma treatment of LFP enhances LIB electrochemical performance, particularly stability over cycling and rate capability. While it is a promising mechanism, it is limited by its multi-species composition, high operating costs, and sometimes restricted treatment. Nonetheless, this approach can be extended to deposition of metallic particles, and depth modulated doping to further improve conductivity, and ion diffusivity of LFP material.

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