Olive lithium iron phosphate (named as LiFePO₄, abbreviated as LFP) is one of the most popular cathode materials for high power lithium ion batteries (LIBs) of the electrical-vehicle (EV), lithium iron phosphate (LiFePO₄, LFP) is limited to its relatively lower theoretical specific capacity of 170 mAh g⁻¹. To break the limits and further improve the capacity of LFP is promising but challenging. In this study, the ball-milling method is applied to the mixture of LFP and carbon, and the effective capacity larger than the theoretical one by 30 mAh g⁻¹ is achieved. It is demonstrated that ball-milling leads to the LFP-Carbon interface to store the excess Li-ions.

**Keywords**: Lithium iron phosphate; ball-milling; interface; excess capacity.

We made new beta-LFP activated to create new diffusion paths and storage sites of Li-ions by ball-milling the nanoparticles with conductive carbon. In this work, ball-milling treatment is applied to the mixture of LFP and acetylene black, and a capacity as high as 200 mAh g⁻¹ is achieved.

LFP was synthesized via solvothermal method. Ferrous sulfate, lithium hydroxide and phosphate acid was dissolved in ethanol glycol separately. A dark green slurry was formed by mixing the solutions. After 2h stirring, to make sure of thorough mixing and heating to 180°C for 8h, product can be collected from centrifugation, washed with water and ethanol and dried at 80°C in vacuum oven overnight. Morphologies of LFP nanocrystals are tested by scanning electron microscopy (SEM) as shown in Fig. 1(b). Synthesized nanocrystals are in shape of nanoparticles with edges and corners, with size of about 80 nm. The X-ray diffraction (XRD) was carried out on Bruker D8 Advance with Cu-Kα radiation, and the result shows that the as-prepared LFP particle are in Pnmb space group (PDF#83-1173). As shown in Fig. S1, it is pure and no other secondary phase exists. High resolution transmission electron microscopy (HRTEM, inset of Fig. 1(b), carried out by FEI Tecnai G2 F30, shows some crystallographic planes of the LFP crystal, and proves particles are monocystal and well crystallized.

The electrochemical tests of the materials were carried out on the coin cells. The samples were dispersed in polyvinylidene fluoride solution. The formed slurry was coated on aluminum foil as cathode and was dried in vacuum oven. The coating weight of the electrode is 1 mg cm⁻². Lithium metal was used as anode and LiPF₆ solution as electrolyte to...
Figure 1(a) shows XRD results of samples with different milling time. It shows that all peaks of LFP remain almost the same positions, in great agreement with standard peak positions from PDF#83-1173. So the structure of LFP does not change during the milling process. Intensity of peaks decreases as milling time increases, which illustrates the degree of crystallinity decreases in the process, which is a common phenomenon in ball-milling treatment.14 As discussed in the following, the defected domains are formed during the ball-milling.

The same ball-milling process as the cathode sample is also applied to carbon black. Figure 2(b) shows that in the voltage range between 2.0 V and 4.2 V, the milled carbon has a capacity of 27 mAh g\(^{-1}\) at the current of 17 mA g\(^{-1}\). With the corresponding capacity of ball-milled carbon excluded, the samples with the ball-milling time of 2, 4, 8, and 10 h have the capacity of 146, 149, 170, and 200 mAh g\(^{-1}\), respectively. The capacity was calculated on the basis of LFP and the capacity corresponding to carbon black has been excluded (calculation method for the effective capacity of the ball-milled LFPC-\(n\) is discussed in detail in the Supporting Information). It means that the effective capacity increases as milling time increases.

The charging/discharging curves of the milled samples LFPC-\(n\) have partial platform with a big slope, which are different from that of LFPC-0 (Figs. 2(a) and 2(b)). Different current are applied to LFPC-10 to test the rate and cycling performance, and it shows great cycling performance with no capacity fading after 1000 cycle at 1 C (170 mA g\(^{-1}\)) as shown in Figs. 2(c) and 2(d). The capacity of the platform part at 3.45 V remains about 70 mAh g\(^{-1}\) and almost does not change as the ball-milling time increases from 2 h to 10 h (Figs. 2(a) and 2(b)). The platform in the charging/discharging curves illustrates that the amount of pure LFP crystal decreased initially in the ball-milling process and remain constant after about 2 h, which means that the initial ball-milling destroys the crystal structure on the outer layer of LFP nanocrystals, and then it reaches equilibrium subsequently. The capacity of the slope part increases as the ball-milling time increases. The slope is partly contributed by the non-oliven phase caused by ball-milling. The non-oliven phase, such as the amorphous LFP, has a high initial capacity close to 170 mAh g\(^{-1}\), but the amorphous often has a relatively bad cycling performance.18 However, the milled samples shows good cycling performance as discussed above, therefore the defective phase may be some special defective phase other than the amorphous one.

Interestingly, LFPC-10 achieved a capacity of 200 mAh g\(^{-1}\), which is larger than LFP theoretical capacity of 170 mAh g\(^{-1}\), meaning that excess Li-ion storage sites are created by ball-milling. Because the capacity of carbon has been excluded, it is speculated that the excess Li-ion storage
Excess lithium storage in LFP-Carbon interface by ball-milling

Sites lie in the LFP-Carbon interface. To better explain excess Li-ion storage sites in the surface, X-ray photoelectron spectroscopy (XPS) is applied to investigate the surface of LFP and carbon black.

XPS test demonstrates that, for LFPC-0, Fe-ions in both the surface and the bulk are bivalence ($\text{Fe}^{2+}$), which is reasonable for lithiated state (Figs. 3(a) and S3(a)). But for the ball-milled LFPC-10, Fe ions in the bulk remains bivalence (Fig. S3(a)), but Fe ions on the surface of the LFPC-10 transforms to trivalence ($\text{Fe}^{3+}$). As shown in Fig. 3(a), the peaks of Fe 2p XPS spectra shifted from 710 eV and 724 eV to higher value 712 eV and 726 eV, respectively. Therefore, Li-ions are extracted from the LFP surface during the ball-milling process. The extraction of Li-ions from the surface is

![Graph showing voltage-capacity curve](image)

**Fig. 2.** Electrochemical test of samples LFPC-\(n\), \(n\) denotes the different ball-milling time. Voltage-capacity curve of (a) first cycle and (b) 5th cycle. (c) Rate performance of LFPC-10 at different current. (d) Cycling performance of LFPC-10 at the current of 170 mA g\(^{-1}\).

![Graph showing rate and cycling performance](image)

![Graph showing XPS spectra](image)

**Fig. 3.** Comparison of XPS spectra between non-milled LFPC-0 and milled LFPC-10. (a), (b), (c), and (d) shows the spectra of Fe 2p, Li 1s, O 1s, and C 1s, respectively.
further proved by Li 1s XPS spectra (Figs. 3(b) and S3(b)), where the peak at 57 eV attributed to Li\(x\)C is detected on the surface. While for the non-milled hLFP-C-0, no Li\(x\)C is detected. This result demonstrates that lithium transfers from LFP to carbon black surface, forming Li–C bond in the ball-milled process. The strong interaction between LFP and carbon black is in agreement with serious aggregation of the particles detected by SEM (Fig. 1(c)).

In addition, it is found that the first charging process of different ball-milled samples exhibit almost the same capacity, although the discharging capacity increases along with the ball-milling time (Fig. 2(a)). It is illustrated that Li-ions extracted from LFP to LFP-Carbon interface is still active and could contribute to the capacity. Smaller nanoparticles, large specific surface area, and more lithium storage sites are provided on the surface.\(^\text{20}\)

Besides, Figs. 3(c) and 3(d) illustrate the O 1s XPS spectra. For the LFPC-0, the O 1s peak is only contributed by LFP. As shown in Fig. 3(c), it is interesting that the O 1s peak of the ball-milled LFPC-10 is asymmetric and a new peak at 533 eV can be detected. The peak is attributed to the C–O or C=O bond, which illustrates the chemical interaction between the carbon and oxygen. On the other hand, the C 1s XPS spectra shows an additional peak around 288 eV, which is also attributed to the C–O and C=O bond, in the ball-milled sample LFPC-10. Therefore, both the O 1s and C 1s XPS spectra demonstrate the presence of C–O or C=O bond after ball-milling. Lung-Hao Hu et al. has reported\(^\text{21}\) that C–O (C=O) bond can provide lithium storage with formation of lithium–oxygen bond, and the reaction voltage was proved to be around 3 V, which is in agreement with electrochemical performance of LFPC-10 in this study.

Given all the results above, it is believed that the ball-milling leads the initially separated LFP and carbon black particles to close contacting with each other, and the chemical interaction between particles creates the LFP-Carbon interface as excess Li-ion storage sites (Fig. 4). It is these Li-ion storage sites that contribute to the excess capacity beyond the theoretical one.

In summary, the ball-milling method is applied to LFP nanocrystals mixed with carbon black. Interestingly, the milled nanocrystals achieved a specific capacity larger than the theoretical value by 30 mAh g\(^{-1}\). The SEM image illustrated that the initially separated LFP and carbon black aggregated after ball-milling, leading to the close contact between the LFP and carbon black nanoparticles. The XPS spectra demonstrated that Li-ions on the LFP surface transformed into the carbon, and the newly formed C–O bonds are detected, which illustrate the chemical interaction between the LFP and carbon black. Therefore, the new LFP-Carbon interface is created. The excess Li-ion storage sites lies in the LFP-Carbon interface and therefore leads to excess capacity beyond the theoretical value.

Fig. 4. Schematic of the process that, after ball-milling, the initial mixture of separated LFP nanocrystals and carbon black transferred into tightly aggregated state with chemical interaction between each other, forming the LFP-Carbon interface wherein lies the active Li-ion sites.
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