

Short communication

Carbon coatings with olive oil, soybean oil and butter on nano-LiFePO₄

Ketack Kim*, Ji Hwa Jeong, Ick-Jun Kim, Hyun-Soo Kim

Battery Research Group, Korea Electrotechnology Research Institute, Changwon, 641-600, Republic of Korea

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Abstract

Kitchen oils (olive, soybean and butter) are selected for carbon coatings on LiFePO₄. The surface properties of LiFePO₄ are unknown or vary depending on synthetic methods. The multi-functional groups of fatty acids in the oils can orient properly to cope with the variable surface properties of LiFePO₄, which can lead to dense carbon coatings. The low price and low toxicity of kitchen oils are other advantages of the coating process. LiFePO₄ ($D_{50} = 121$ nm) combined with the carbon coating enhances the rate capability. Capacities at the 2C rate reach 150 mAh g⁻¹ or higher. The charge retention values of 2.0C/0.2C are between 94.4 and 98.9%.

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1. Introduction

As the demand for powerful and large Li-ion batteries grows, LiFePO₄ has received much attention as a positive electrode (cathode) material due to its high stability. Ever since it was introduced by Radhi et al. [1], many efforts have been made to enhance its low conductance. Among the ways proposed to achieve this, carbon coatings are considered to be promising [2–5].

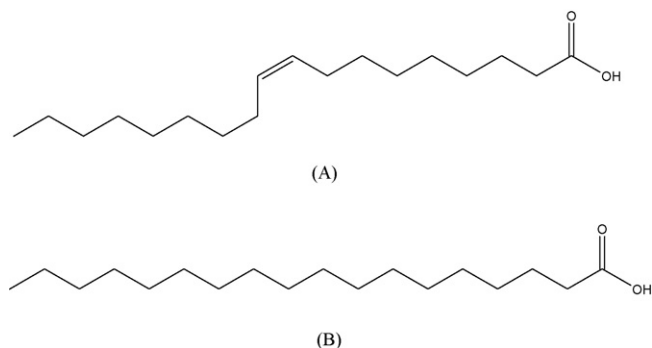
When slurries for the cathode are made, carbon powder (conductive material) does not guarantee good electrical contact with all the active material particles, because the active material may not be fully covered with the carbon powder. Some particles may be isolated from others, while others may be only partly covered with carbon. Prior to making the slurry, the carbon coating on the active material can be processed to make better electrical contact among the particles. The coating can remarkably reduce ‘dead zones’ where active particles are coagulated or poorly networked with the carbon.

Typically, a small amount of carbonaceous materials are mixed with the active material, followed by sintering of the mixture under inert gas. Any carbon coating can improve the conductance tremendously, regardless of the quality. Several conditions need to be improved for real applications, however,

such as the ratio of the active material, the thickness of the electrodes, the densities of the coatings and so on. In order to improve these factors, one needs to consider the surface interaction between the carbonaceous and active materials before furnace treatment.

In the step that produces a homogeneous carbon coating, the active material is evenly soaked with a solution of the carbonaceous material. The latter material approaches the surface of LiFePO₄ with its functional groups properly oriented. The conformation between LiFePO₄ and the carbonaceous material greatly affects the quality of the coating. If the LiFePO₄ interacts favourably with the carbonaceous material, this solution–solid interaction may lead to a high-quality carbon coating when it is sintered. On the other hand, if the surface interaction is not favourable, the quality and density of the carbon coating may be damaged. The surface properties of LiFePO₄ are unknown, and they vary depending on how the material is treated during the synthetic and coating processes. For example, LiFePO₄ could be polar, non-polar, hydrophobic or hydrophilic. Carbonaceous materials that have multiple functional groups can favourably interact with LiFePO₄ regardless of these various properties. A material that can interact with all of these random properties could be soap. The raw materials of soaps are fatty acids or surfactants. Kitchen oils such as olive oil, soybean oil, and butter are chosen in this study in which the main ingredients are fatty acids. Their low toxicity and low price are further reasons for their selection.

* Corresponding author. Tel.: +82 55 2801665; fax: +82 55 2801590.
E-mail address: kkim@keri.re.kr (K. Kim).



Scheme 1. Fatty acids in kitchen oils: (A) oleic acid and (B) stearic acid.

Scheme 1 shows the two main ingredients in kitchen oils, namely, oleic acid and stearic acid. Both have the same carbon number, 18, and have 2 oxygen atoms. Except for a double bond in oleic acid, they are very similar, and look like a carbon tape when oxygen and hydrogen atoms are removed.

Scheme 2 shows how fatty acids can interact with the active particles. Scheme 2A and B are micelle and reverse micelle interactions. Scheme 2C may occur when LiFePO_4 attracts the carbon chain, or when the repulsion strength is too weak and carbon skeletons wrap around the core. The fatty acids interact with LiFePO_4 through any type of model depending on the surface properties of LiFePO_4 and the solvent used in the soaking procedure. This is called the ‘active interaction model.’ In this study, the aim is to demonstrate the possibility of using kitchen oils as a carbon coating material. Also, carbon coatings combined with nano-particles are discussed.

2. Experimental

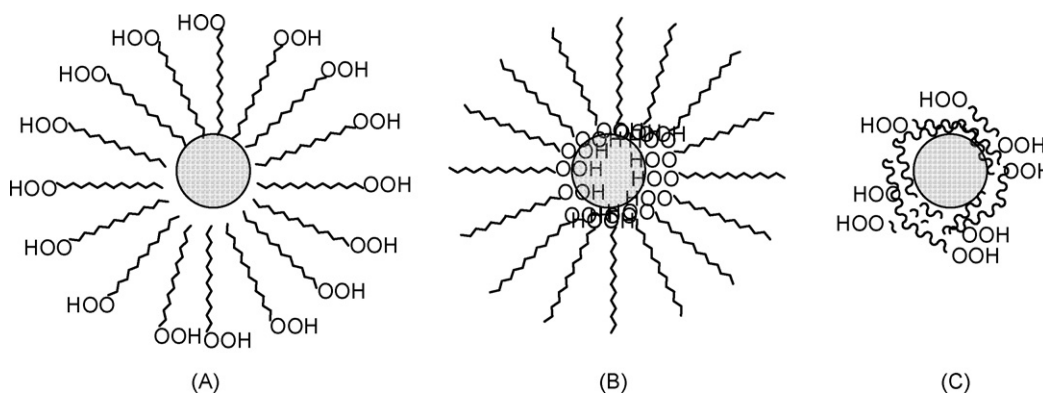
LiFePO_4 was obtained from Phostech Lithium, Inc. 1.0 M LiPF_6 in ethylene carbonate/diethyl carbonate (EC/DEC) = 1:1 by volume was obtained from Techno Semichem. Co., Ltd. Poly(vinylidene fluoride), PVdF, was purchased from Aldrich. *N*-methyl-2-pyrrolidone (NMP) was obtained from Junsei Chemical. In order to prepare nano- LiFePO_4 , the powder was ball-milled for weeks in ethanol. The size distribution of the powder was measured with a particle-size analyzer (LS230, Coulter). Two different nano- LiFePO_4

powders were prepared. The D_{50} values of each powder were 250 nm ($D_{10} = 130$ nm, $D_{50} = 250$ nm, $D_{90} = 470$ nm) and 121 nm ($D_{10} = 97$ nm, $D_{50} = 121$ nm, $D_{90} = 167$ nm). Images of the LiFePO_4 powders were taken with a Hitachi SE-4800 field emission scanning electron microscopy (FE-SEM).

Coating materials were premixed with the nano- LiFePO_4 in isopropyl alcohol before sintering the mixture at 550 °C for 1 h under argon. The coated carbon content was measured with a thermogravimetric analyzer (TGA, TA instruments, Q100) [6]. The prepared LiFePO_4/C was well mixed with super black P and PVdF at a ratio of 85:8:7 in NMP to make the slurry for the cathode. The ratio applies to all measurements unless stated otherwise. A Li foil served as the anode. 2032 type coin cells were prepared to monitor the performance of the materials. A 15- μm thick separator was placed between the two electrodes. All cell preparations were performed in a dry room in which the water content was maintained below 10 ppm.

3. Results

Prior to milling the grains of LiFePO_4 , their particle size was measured and found to be nearly 6 μm in diameter. Carbon was detected on the LiFePO_4 in the range of 1.0–1.5%. It delivers nearly 145 mAh g^{-1} at 0.2 C. The data in Fig. 1 was obtained from 250 nm LiFePO_4 that was not carbon-coated. Its original carbon coating was removed by ball-milling. The active material shows poor capacity in Fig. 1A. Its discharge capacity is 43 mAh g^{-1} . More carbon was added (12%) in order to increase the conductor content of the cathode. The results in Fig. 1B show that the higher carbon content increases the capacity to 65 mAh g^{-1} . It is estimated that 25–30 wt.% carbon in the cathode is necessary to reach 140–160 mAh g^{-1} without a carbon coating. The nano-powder’s large surface area requires more carbon than a micron-powder to cover the surface. Because the intrinsic conductivity of LiFePO_4 is extremely low, each particle of LiFePO_4 needs to be well connected with conductor material. Scanning electron micrograph of 250-nm LiFePO_4 particles are given in Fig. 2. Any changes produced by the carbon coatings are not identified in the images. Coagulation occurs due to the high interaction strength of the nano-particles. The rate capability of a carbon-coated material is shown in Fig. 3. A 3 wt.% olive oil was added to the active material to be sintered, resulting



Scheme 2. Interaction models between LiFePO_4 and fatty acids. The core is LiFePO_4 .

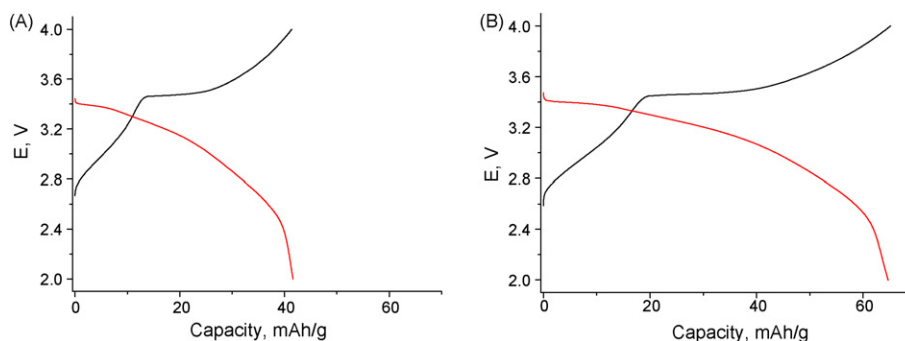


Fig. 1. Discharge curve of bare 250-nm LiFePO_4 at 0.2C. Composition ratio of LiFePO_4 :conductor:binder for: (A) 85: 8: 7 and (B) 81:12: 7.

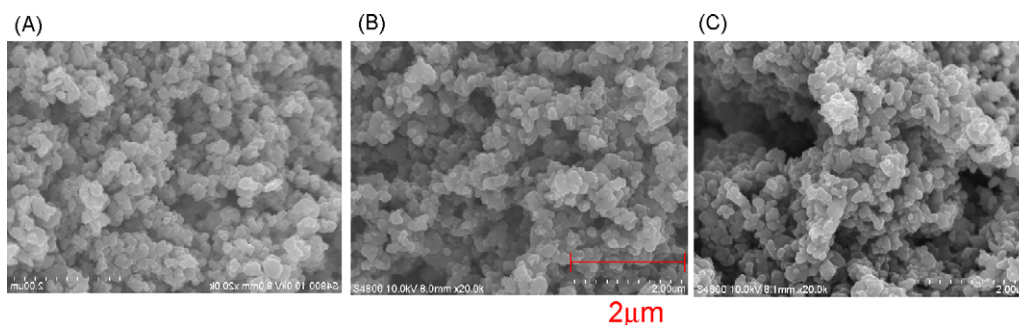


Fig. 2. Scanning electron micrographs of 250-nm LiFePO_4 : (A) bare LiFePO_4 , (B) 3 wt.% olive oil added LiFePO_4 , (C) 5 wt.% olive oil added LiFePO_4 .

in a 1.6% carbon coating on the material. The limiting potential of the charging cycles was extended from 4.0 V (Fig. 3A) to 4.2 V (Fig. 3B) and 4.5 V (Fig. 3C). The performance in Fig. 3B and C does not show a higher capacity or a better rate capability than that in Fig. 3A. The capacities are not charging–time

(voltage) dependent. Regardless of the charging time or voltage, the particles are still too large to allow migration of the lithium ion. This large size strongly affects the resistance that is observed at the potential values of each discharge rate. Higher rates obviously show higher IR drops. The IR drop and relatively low capacity are ascribed not only to the large grains but also to coagulation of the grains after carbon coating. A 5 wt.% olive coating presents a rather shorter potential plateau near 3.4 V and a poorer rate capability than a 3 wt.% olive oil coating, as seen in Fig. 4. It is concluded that the coagulation problem is the main reason/cause of the decrease in performance when an excess carbon coating is formed. Coagulation results in a lowering of the density of LiFePO_4 , which leads to an uneven distribution and a low packing density of the active material [7].

The rate capability curves for 3 wt.% olive oil coated on 121-nm LiFePO_4 are presented in Fig. 5. A clear improvement is seen with this size over the 250-nm size. Comparing with Fig. 3, the IR drop of 120-nm LiFePO_4 is diminished due to its smaller size [3,8–10]. The Capacity at 0.2 C for each cut-off potential is 162.0, 161.8 and 163.3 mAh g^{-1} for 4.0, 4.2 and 4.5 V, respectively. By contrast, the capacity at 2.0 C for each cut-off potential is 149.9, 152.8 and 153.3 mAh g^{-1} for 4.0, 4.2 and 4.5 V, respectively. Thus, the capacities tend to increase slightly as the cut-off voltage rises. The data in Fig. 5B show 94.4% of charge retention at a 2C versus a 0.2C rate. As the size of LiFePO_4 becomes smaller, Li ions utilize a higher volume% of the active material grains than larger LiFePO_4 grains. The 121-nm LiFePO_4 is about one-eighth the size of 250-nm LiFePO_4 in volume. In other words, the 121-nm size is small enough to exhibit some capacity enhancement by a longer charging time. Perhaps parti-

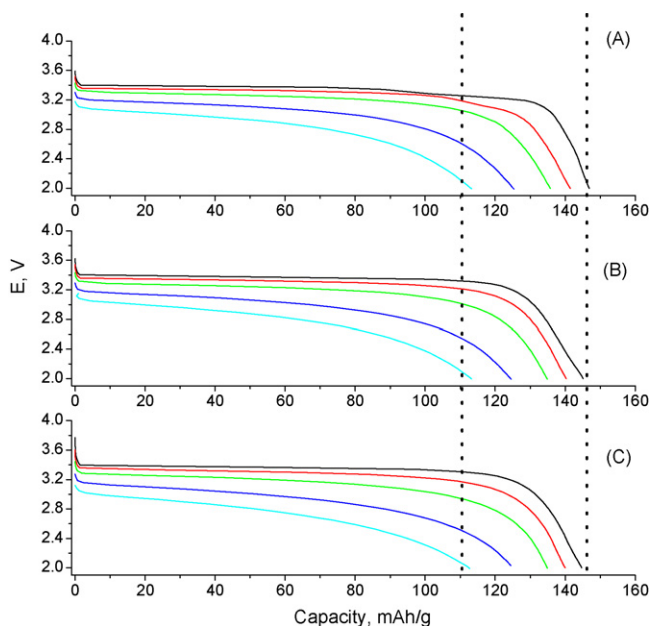


Fig. 3. Discharge curves of 3 wt.% olive oil added 250-nm- LiFePO_4 . Limiting potential of all discharge cycles is 2.0 V. Limiting potentials of charge cycles: (A) 4.0 V, (B) 4.2 V, and (C) 4.5 V. Discharge rates for each curve from right to left are 0.2, 0.5, 1, 2, and 3C.

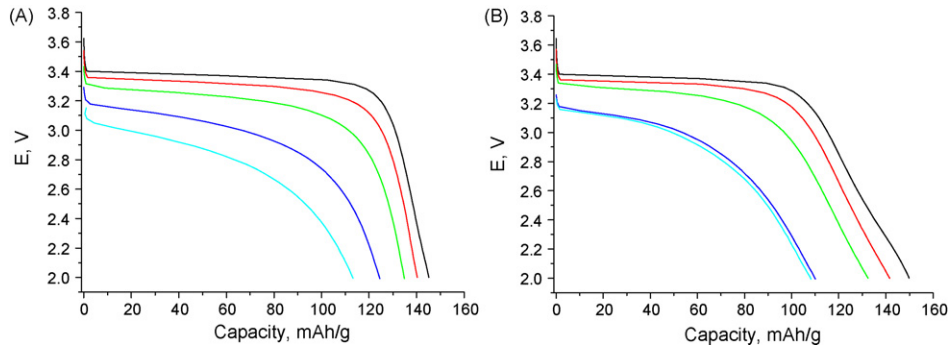


Fig. 4. Comparison between 3 wt.% and 5 wt.% olive oil added 250-nm LiFePO₄: (A) 3 wt.% olive oil, (B) 5 wt.% olive oil. Limiting potentials are 2.0 and 4.2 V.

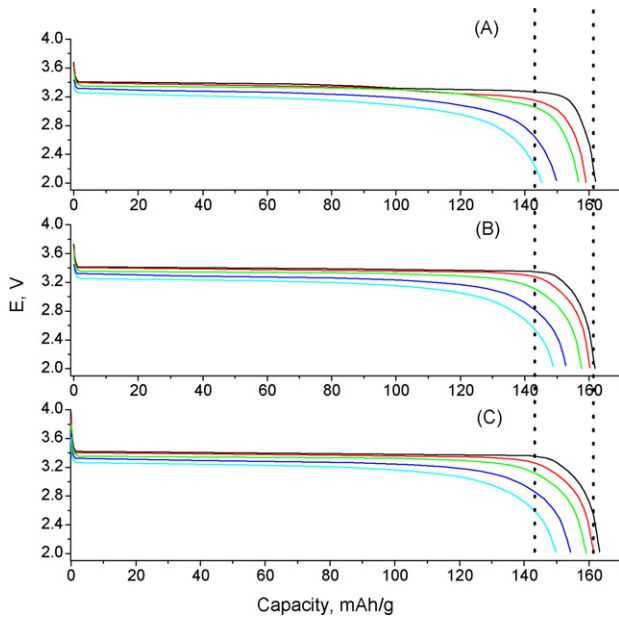


Fig. 5. Discharge curves of 3 wt.% olive oil added 121-nm LiFePO₄. Limiting potential of all discharge cycles is 2.0 V. Limiting potentials of charge cycle: (A) 4.0 V, (B) 4.2 V, (C) 4.5 V. Discharge rates for each curve from right to left are 0.2C, 0.5C, 1C, 2C, and 3C.

cles that are smaller than 121 nm may be even more efficient in terms of utilization of the whole volume of the LiFePO₄ grains. Grains smaller than 100 nm were not, however, studied.

In Fig. 5C, multiple potential scans between 4.5 and 2.0 V do not show any abnormal features that can be observed at cobalt-based cathode materials. There may be more chance to detect

electrolyzed products from electrolytes under this condition. The electrode showed, however, stable and excellent performance at high potential.

Soybean oil and butter were also utilized as carbon coating materials. A 3 wt.% of the oils were added to 121-nm LiFePO₄ and the rate capability curves are given in Fig. 6. The capacity values for the butter coating in Fig. 6A are 153.8 mAh g⁻¹ for 0.2C and 152.0 mAh g⁻¹ for 2.0C. Hence, the capacity ratio of 2.0C/0.2C is 98.9%. The rate capability is better than that of olive oil. The capacities are lower at all charging rates than those for olive oil. The capacities from soybean oil are 159.3 mAh g⁻¹ for 0.2C and 156.5 mAh g⁻¹ for 2.0C. Thus, the capacity ratio of 2.0C/0.2C is 98.2%. This is comparable with that of the olive oil coating. The soybean oil coating gives a higher capacity than butter, and its value is lower than that of olive oil. The thickness of the electrodes coated with olive oil, butter and soybean oil is 40, 36 and 25 μm, respectively. It is not fair to say that any of these electrodes is better than the others because of the thickness variation. However, coatings with these oils provide competitive and better data than other reported values [7,11,12]. The difficulty in controlling the electrode thickness arises from both the hand-cast method and the various viscosities of the slurries made by the different coating oils. Performance at the 0.2C rate for charge and discharge cycles is given in Fig. 7. The thickest electrode with olive oil gives higher values than the other coatings. The charge retention after 48 cycles is 93.7%. The curves for the other electrodes are almost parallel to that of the olive oil coated one. This behaviour curve also implies that the electrodes coated with olive oil, butter or soybean oil are comparable.

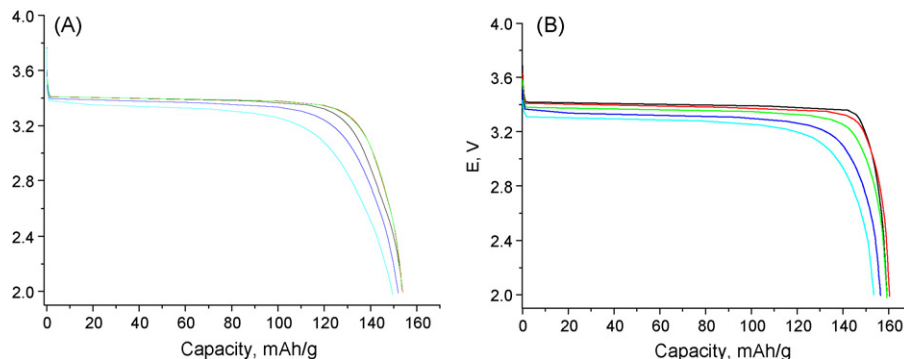


Fig. 6. Discharge curves of 3 wt.% butter, soybean oil added 121-nm LiFePO₄. (A) butter, (B) soybean oil. Limiting potentials are 2.0 and 4.2 V.

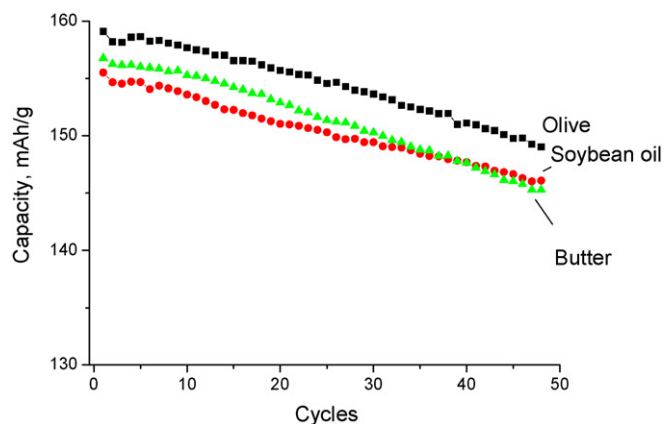


Fig. 7. Cycles of 3 wt.% olive, butter, and soybean oil added 121-nm LiFePO₄. Limiting potentials are 2.0 and 4.0 V.

4. Discussion

Kitchen oils serve as very good coating materials. The quality of the coatings and the small LiFePO₄ grain size combined to deliver good capacity and rate capability. Huang et al. [3] coated 15% carbon on 100–200 nm particles. The coating was formed from a carbon gel. A capacity of 120 mAh g⁻¹ was obtained at 5C. A well-optimized performance with 18,650 type cells showed the possibility of making batteries with 80 wt.% LiFePO₄ [10]. A synthetic method for narrow particle distribution can lead to very good performance with 80 wt.% LiFePO₄ [13]. The coated materials in this study give data that is competitive with those earlier studies. The mass of LiFePO₄ in the electrode lies between 82 and 83 wt.%. Although the active interaction model appears to provide a very effective method for carbon coating; more work is necessary to achieve better performance and lower cost.

It is found 250 nm particles are still too large to reach 90% of 2.0C/0.2C charge retention. Also, it appears that a 250 nm-depth is too long for the migration of Li ions. Extending the charging time exerts little effect on the discharge capacity. A 121-nm diameter gives more discharge capacity when it is charged more. When nano-synthetic methods can provide inexpensive tiny particles smaller than 100 nm, the coating methods adopted in this study could be a more attractive approach to improve both performance and cost. It is observed that an excess carbon coating deteriorates the electrochemical performance by lowering the quality and the packing density of the electrode. Studies are

underway to reduce both the coating thickness and the conductor content in the electrodes. Studies with fatty acids in the oils are on-going, and will investigate the role of double bonds and the dependence of the chain length of fatty acids. Among the models in Scheme 2, it is considered that Scheme 2C may provide compact carbon coatings that are better than the models in Scheme 2A and B. Further studies with each fatty acid can provide more ideas about the interaction models.

5. Conclusions

Carbon coatings with kitchen oils provide competitive performance compared with other carbon coatings and particle-size engineering. These oils are cost-effective and environmentally benign. Carbon coated on to 121-nm LiFePO₄ show very good performance. Capacities at the 2C rate with the coatings reach 150 mAh g⁻¹ or higher. The charge retention values of 2.0C/0.2C are between 94.4 and 98.9%. These high charge retention values demonstrate that the active interaction model with kitchen oils (fatty acids) works well with LiFePO₄.

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