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Direct regeneration to prepare lithium iron phosphate cathode material from spent $LiFePO_4$ batteries via sol-gel method

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Abstract

Developing sustainable recycling methodologies becomes imperative with the escalating global consumption of lithium-ion batteries (LIBs) in electric vehicles (EVs). Aside from developing new materials for lithium-ion batteries, the regeneration of spent lithium-ion batteries is also of great interest owing to the rising concern of environmental conservation. This study presents a pioneering approach that involves the direct regeneration of spent $LiFePO_4$ via a novel sol-gel method. The effect of varying the calcination temperature of the $LiFePO_4$ was investigated via various structural and electrochemical analyses. The results from Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD) analysis revealed that an elevation in temperature significantly enhances the structural integrity and morphological characteristics of the regenerated $LiFePO_4$, as well as the phase purity of the material. Electrochemical evaluations on the regenerated $LiFePO_4$ demonstrated an elevated electrochemical performance compared to the spent $LiFePO_4$. The findings of this research reveal the optimal calcination temperature suitable for the direct regeneration of spent $LiFePO_4$ via the sol-gel method.

Keywords: Lithium-ion Batteries, $LiFePO_4$, Spent $LiFePO_4$, Direct Regeneration, Sol-Gel Method

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1. Introduction

Recently, there has been a significant shift towards electric vehicles (EVs) in response to growing environmental concerns. This shift is largely fueled by advancements in lithium-ion battery (LIB) technology due to its high energy density, extended cycle life, and significant capacity [1]. According to market share forecasts, automotive lithium-ion (Li-ion) batteries experienced a substantial rise of approximately 65% in 2022, reaching 550 GWh from roughly 330 GWh in 2021. In addition, the worldwide demand for lithium-ion batteries was predicted to ascend to 658 GWh by 2023. there is an expected growth rate in production capacity of 59% from 2023 to 2028, primarily propelled by the burgeoning electric vehicle market [2,3]. These trends underscore the considerable potential of these batteries to have a profound influence, particularly as critical contributors to the advancement of sustainable energy solutions. Nevertheless, in the context of lithium-ion batteries, the cathode material emerges as a crucial component, largely due to its significant impact on both the weight and cost of the batteries compared to anodes. Lithium iron phosphate (LFP, LiFePO4) is a material of significant interest within the broad spectrum of cathode materials employed in lithium-ion batteries. They were characterized by long cycle life, inherent thermal safety, high stability, and environmental benignity, making them an attractive option for EV applications. However, as the global consumption of lithium-ion batteries escalates, an efficient recycling method becomes indispensable to handle the increased volume of spent lithium-ion batteries and minimize their environmental impact [4].

Existing regeneration methods are broadly classified into pyrometallurgical, hydrometallurgical, and direct recycling processes. Pyrometallurgical processes involve high-temperature operations for metal recovery but suffer from high energy requirements, the potential release of toxic gases, and the inability to maintain the unique structural advantages of $LiFePO_4$. Hydrometallurgical processes employ aqueous solutions to extract valuable elements; however, these processes face limitations due to significant water usage, the need for strong acids or bases, and challenges related to liquid waste management. In contrast, direct recycling processes directly recover and regenerate spent cathode materials such as $LiFePO_4$, preserving their structural and compositional characteristics and facilitating their direct reuse in new battery production. Unlike pyrometallurgical and hydrometallurgical methods, direct recycling avoids the dissolution or decomposition of cathode material, conserving its inherent properties [5,6].

This research introduces an innovative methodology involving the direct regeneration of spent $LiFePO_4$ using a novel sol-gel process. Direct recycling aligns well with promoting the reuse of resources, reducing waste, and contributing to sustainability in the burgeoning EV and lithium-ion battery industries. This study aims to refine this direct regeneration method, specifically examining the influence of calcination temperature on the structural and electrochemical properties of regenerated $LiFePO_{4.}$

2. Materials and Methods

2.1 Materials

lithium hydroxide anhydrous (LiOH, 98% purity, Alfa Aesar), citric acid anhydrous (C_6H_8O7, 99.5% purity, JT Baker), ethanol (C_2H_5OH, 95% purity, Echo) were of analytical grade and used without further purification. All solutions were prepared using deionized water, purified by an ultimate water purification system (PURELAB Maxima, ELGA)

2.2 Preparation of spent $LiFePO_4$ powder

The spent lithium-ion batteries employed in this study were sourced from a commercial company in Taiwan. The batteries were first discharged in a saturated NaCl solution for 72 hours. After that, the batteries were dismantled in the packaging and shell in the glove box, leading to the disassembly of key components such as the separator, anode, and cathode plates. The cathode plates were then fragmented into smaller pieces and submerged in hot water. This process expedited the separation of cathode and anode scrap from their respective aluminum (Al) and copper (Cu) foils, thereby enabling automatic separation. Finally, the cathode scrap was ball-milled to form spent cathode powders and dried at 60°C for 24 hours to eliminate moisture.

2.3 $LiFePO_4$ regeneration process

The regeneration process of $LiFePO_4$ was initiated by preparing a solution with 1 mol of lithium hydroxide (LiOH) dissolved in water. This solution was then modified by adding citric acid in varying molar ratios of 2, 3, and 4. Each mixture was stirred at room temperature for 10 minutes. Subsequently, 1g of spent $LiFePO_4$ was added to the solution. Three samples were prepared, each with a unique molar ratio of spent $LiFePO_4$, LiOH, and citric acid, being 1:1:2, 1:1:3, and 1:1:4, respectively. These solutions were then subjected to a ball-milling process. After that, the solutions were stirred on a hot plate at a temperature of 100°C until a sol-gel was formed. These sol-gel samples were then dried at 80°C for 24 hours. Subsequently, the dried samples underwent calcination within a furnace at temperatures ranging from 400°C to 700°C under a nitrogen-inert atmosphere. The calcinated samples were washed in water and ethanol to remove impurities. They were then dried at 80°C for 24 hours. This systematic process served as the basis for the regeneration of spent $LiFePO_4$. The resultant material served as the subject of further investigation.

2.4 Characterization

A myriad of analytical methodologies was applied to characterize the regenerated $LiFePO_4$. An X-ray diffraction spectrometer (XRD, MiniFlex, Rigaku) with Cu-Kα radiation ($\lambda = 1.54$ Å) was utilized for the structural evaluation. Data were collected using a step scan of 0.02°, a scanning speed of 20°/min, and a 2θ scanning angle range of 10 to 70°. Scanning electron microscopy (SEM, JSM-7610F, JEOL) was employed to scrutinize the morphology of samples, with a gold film applied to enhance electrical conductivity.

2.5 Electrochemical performances

To assess the electrochemical performance, CR2032-type coin cell half-cells were fabricated, using $LiFePO_4$ samples as the cathode material and lithium metal as the anode material. This assembly process was conducted in an argon-filled glove box. During the cell production, 1 M $LiPF_6$ solution dissolved in a mixture of ethyl carbonate and dimethyl carbonate with a conductive agent (super P) and binder (PVDF). The charge-discharge performance analysis and the cycling characteristics were examined using a BT-2000 battery test system by Arbin.

3. Results and Discussion

3.1 X-ray diffraction analysis

The X-ray diffraction patterns of $LiFePO_4$ samples calcined at temperatures ranging from 400 to 700 °C with a concentration of 2 mol of citric acid are demonstrated in Fig. 1a. The XRD investigation revealed that at a calcination temperature of 400°C, impurities including $FePO_4$ and Fe_2O_3 were identified in the regenerated $LiFePO_4$ [7,8]. Elevating the calcination temperature to 500°C effectively reduced some of the $FePO_4$ impurities, but a certain proportion of impurities remained. Furthermore, the $FePO_4$ phase was still present between the temperatures of 500 and 600°C due to insufficient calcination for Li replenishment and incomplete relithiation reaction. After raising the calcination temperature to 700°C, the successful formation of the $LiFePO_4$ phase was achieved with 2 mol of citric acid, facilitated by an appropriate temperature and sufficient carbon content to allow relithiation reactions. As shown in Fig. 1b, impurities in $LiFePO_4$ samples calcined at 700 °C were eliminated, and the heightened peak intensity of the olivine $LiFePO_4$ phase (Pnma space, JCPDS NO. 40-1499) with the increase in calcination temperature. Fig. 2a depicts the X-ray diffraction patterns of samples synthesized at 700°C with different molar ratios of citric acid. The results indicated the presence of the olivine $LiFePO_4$ phase in all the samples tested. However, an increase in citric acid to 4 mol was associated with the formation of impurities like Li_3PO_4 and $FePO_4$. Similarly, these contaminants were observed in the 3 mol citric acid sample. Conversely, a sample with 2 mol of citric acid exhibited a pure $LiFePO_4$ phase without any detectable impurity phases. Moreover, as shown in Fig. 2b, an increase in citric acid concentration in the sol-gel solution resulted in a more substantial in situ production of carbon during the calcination process. This enrichment of carbon content provokes a partial transmutation of Fe^{3+} to Fe^{2+}, facilitating the formation of olivine $LiFePO_4$ phases and inhibiting the emergence of impurities.

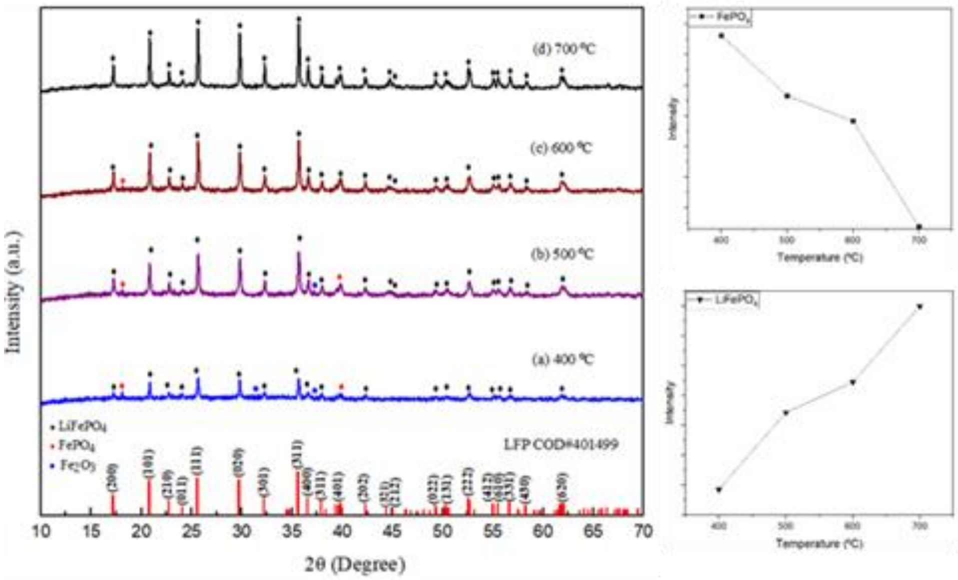

Figure 1. (a) XRD patterns of samples calcined at 400°C, 500°C, 600°C, and 700°C. (b) Comparison of diffraction peak intensities for LiFePO4 at 20.82° and FePO4 at 18.10°.

3.2 SEM analysis

The structure and morphologies of regenerated $LiFePO_4$ at 400 to 700 °C with 2 mol of citric acid were characterized using scanning electron microscopy (SEM). The morphology of regenerated $LiFePO_4$ at 400 °C obtained from

SEM (Fig. 3a) revealed that the regenerated $LiFePO_4$ at 400 °C primarily consisted of irregular particles, with sizes varying from 100 to 800 nm. These particles exhibited significant surface cracking, agglomeration, floccules, and residual PVDF binder. The irregularity of the particle size in regenerated $LiFePO_4$ at 400 °C and its observable structural deficiencies are postulated to arise due to an incomplete relithiation reaction. The limited calcination temperature adversely affects the stability of the lattice structure. Furthermore, the incomplete reintegration of lithium ions into this lithium-depleted compound contributes to particle pulverization and a perceptible decrease in the electrochemical activity of the material.

However, the regeneration process significantly improves its structure and performance. As depicted in Fig. 3b, the regenerated $LiFePO_4$, treated at 700 °C with 2 moles of citric acid, showed a repaired and more uniform structure. Particle sizes ranged between 100 to 1300 nm, agglomeration was no longer present, and there was an apparent decrease in residual decomposition. The structural regeneration is postulated to enhance Li^+ transportation during the charge and discharge cycles, subsequently boosting the electrochemical performance of regenerated $LiFePO_4$. Furthermore, the particle size of the regenerated $LiFePO_4$ at 700 °C is larger than the regenerated $LiFePO_4$ at 400 °C, implying a successful relithiation reaction process. Additionally, the regeneration process incorporates a carbon layer from citric acid. This layer is anticipated to significantly enhance the electric conductivity of the cathode material while also contributing to the increase in the size of crystalline particles. In conclusion, the regenerated $LiFePO_4$ exhibits a significant enhancement in both structure and performance when compared to regenerated $LiFePO_4$ at 400 °C [9].

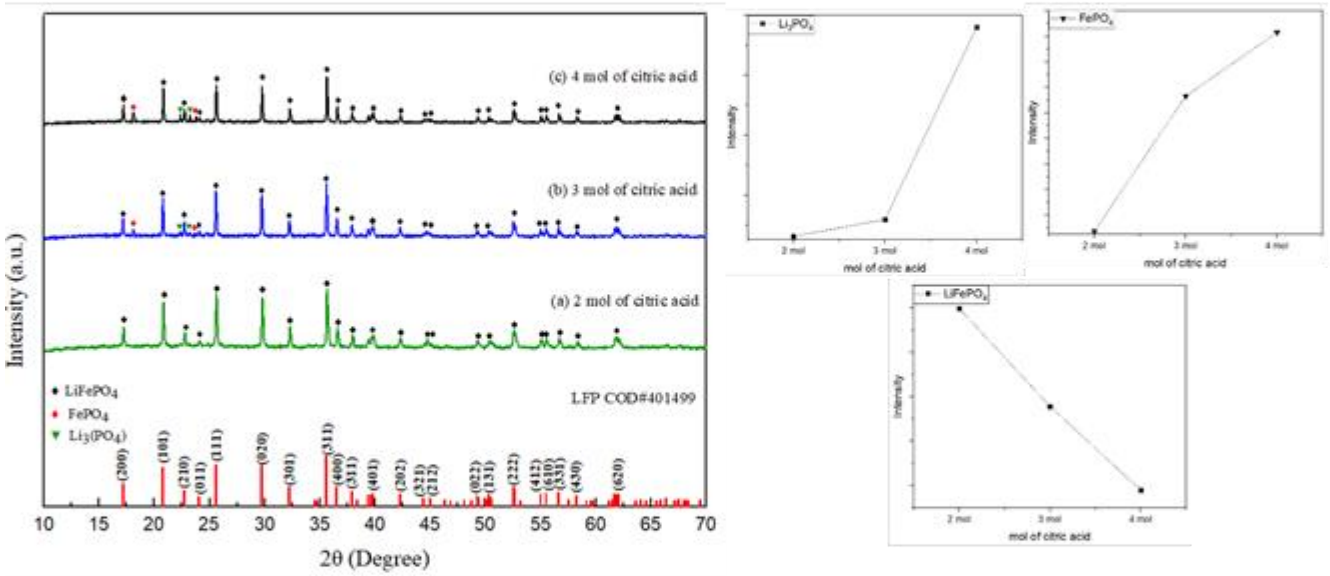

Figure 2. (a) XRD patterns for samples calcined at 700°C with 2 mol, 3 mol, and 4 mol of citric acid. (b) Comparison of diffraction peak intensities for $LiFePO_4$ at 20.82°, Li_3PO_4 at 22.36°, and $FePO_4$ at 18.10°.

3.3 Galvanostatic charge-discharge analysis

Fig. 4 delineates the galvanostatic charge-discharge curves for regenerated $LiFePO_4$ materials, synthesized under conditions of 2 mol of citric acid at a calcination temperature of 700 °C. The specific discharge capacity of the regenerated $LiFePO_4$ sample was measured to be 135.23 mA h/g at 0.2C. This represents an enhancement in comparison to the spent

LiFePO4 sample, which has been previously reported with a specific discharge capacity of 124.35 mA h/g at 0.2C by Li et al. [10] and 114.2 mA h/g at 0.2C by Zou et al. [11]. The variations in these reported values highlight the diverse conditions under which the spent LiFePO4 is processed and its resulting capacities. Hence, it can be inferred that the proper ratio of citric acid and the correct calcination temperature are essential elements influencing the electrochemical performance of the directly regenerated $LiFePO_4$.

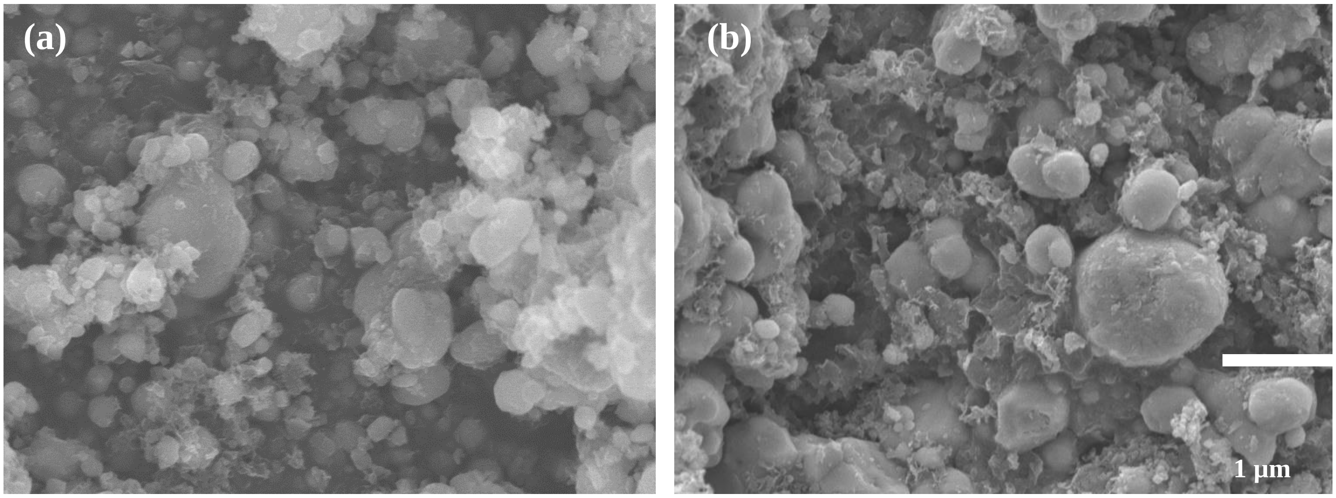

Figure 3. SEM images of regeneration $LiFePO_4$ at (a) 400 °C with 2 mol of citric acid and (b) 700 °C with 2 mol of citric acid.

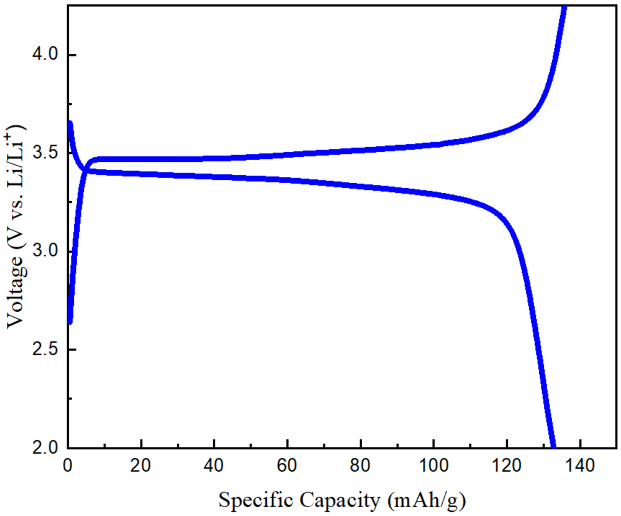

Figure 4. Charge-discharge curves of regenerated $LiFePO_4$ at 0.2C.

3.4 Rate capability analysis

The comparison of the rate capability performance between regenerated $LiFePO_4$ materials synthesized under conditions of 2 mol of citric acid at a calcination temperature of 700 °C, was illustrated in Fig. 5. It is noteworthy that the regenerated LiFePO4, synthesized at a calcination temperature of 700°C with 2 mol of citric acid, exhibited a discharge capacity of 135.23 mA h/g at a 0.2C rate, 127.52 mA h/g at a 0.5C rate, 112.17 mA h/g at a 1C rate, 88.94 mA h/g at a 2C rate, and 45.80 mA h/g at a 5C rate. These results provide significant evidence for the successful recovery of discharge capacity from spent $LiFePO_4$ through relithiation reaction.

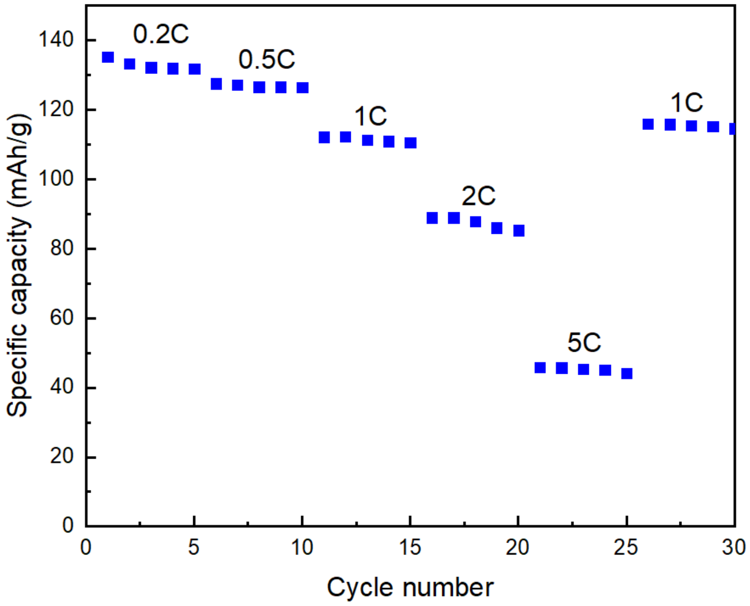

Figure 5. Rate capability performance of regenerated $LiFePO_4$.

4. Conclusions

In conclusion, using the sol-gel method, this study has illuminated a novel process to regenerate spent LiFePO4 cathode material directly. The approach successfully transformed the $FePO_4$ in spent cathode materials into a pure olivine $LiFePO_4$ phase with enhanced structure and performance under suitable conditions, precisely a calcination temperature of 700°C and a citric acid concentration of 2 mol. X-ray diffraction analysis evidenced the formation of a pure $LiFePO_4$ phase with no detectable impurities under these conditions. Scanning Electron Microscopy (SEM) analysis further substantiated these findings by illustrating a repaired and more uniform structure in the regenerated LiFePO4 at 700°C and a citric acid concentration of 2 mol, resulting in an enhanced electrochemical activity. The electrochemical performance evaluation of the regenerated $LiFePO_4$ exhibited a specific discharge capacity of 135.23 mA h/g, representing an enhancement compared to the spent $LiFePO_4$. Moreover, the rate capability analysis demonstrated successful recovery in the regenerated $LiFePO_4$. Overall, using the sol-gel method, the direct regeneration of LiFePO4 cathode material from spent LiFePO4 batteries offers a promising approach to sustainable battery recycling. The study highlights the importance of optimizing the calcination temperature and citric acid concentration to improve the regenerated material's structural and electrochemical properties. Further research on the regeneration process can contribute to developing efficient and environmentally friendly recycling methods for lithium-ion batteries, supporting the advancement of sustainable energy solutions in the electric vehicle and lithium-ion battery industries.

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