

Characteristics of Carbon from Chitin-coated LiFePO₄ and its Performance for Lithium Ion Battery

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A LiFePO₄ battery is the best device for energy storage. Batteries are currently being developed for higher capacity using novel materials. Carbon is one material that can be used to improve the properties of LiFePO₄ batteries. The chitin produced from shrimp shell is a viable material that can be transformed into organic carbon. The chitin is revealed to be an element of 36.6 wt% carbon (C). Carbon is formed of small crystallites comprising electrode composite with a uniform carbon coating that can improve the electrochemical activation for LiFePO₄/C composites. When the electrochemical reaction was operated at 1.2 V, the flow rate was increased 80%. The average charge-discharge capacities were 100 and -100 mAh/g, respectively, while the average energy density over a period of 20 cycles was 336 Wh/kg (maximum ~350 Wh/kg). Therefore, organic carbon can be used to remarkably improve the properties of LiFePO₄ batteries with low-cost materials.

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INTRODUCTION

Presently, the best kind of battery is made of lithium iron phosphate (LiFePO₄). Such batteries can be applied to many technologies for the most sustainable energy storage due to their properties and functions. There are many factors, such as preparation, materials, and methodologies that need to be developed for higher performance lithium ion batteries. Generally, the structure of a lithium ion battery consists of a cathode, electrolyte, and anode, which researchers can develop separately. The specific preparation methodologies, as well as the materials used for the development of cathode, anode, and electrolyte, greatly influence the properties. Today, technologies should be considered using environmentally friendly biomaterials to reduce waste in the future. An example is an additive of free gelatin based on the sol-gel procedure, which has been developed to synthesize LiFePO₄/C powders. Gelatin is a biomaterial that is commercially available, cheap, and environmentally friendly, obtained from the hydrolysis of collagen (Gao *et al.*

2014), while activated carbon from coconut shell is fabricated for electrodes in electric double-layer supercapacitors (Chopngam *et al.* 2021).

The cathode materials used for LiFePO₄ can perform at high voltage (~3.4 V vs. Li/Li⁺) (Liu *et al.* 2018) and possess high theoretical capacity (~170 mAh/g). Other desirable properties include avoidance of environmental pollution, low cost, thermal energy stability, and a long-life cycle (Aravindan *et al.* 2015; Kim *et al.* 2019). Moreover, LiFePO₄ comprises Fe element that is of low cost and readily available in the market, though it has disadvantages, including low conductivity (~10⁻⁹ to 10⁻¹⁰ S/cm), low Li⁺ ion diffusivity (~10⁻¹⁴ to 10⁻¹⁶ S/cm²) (Lu *et al.* 2008; Wang and Sun 2012; Zaghbi *et al.* 2013), and low tap density (Wang and Sun 2012; Zaghbi *et al.* 2013). Many researchers are currently attempting to improve the conductivity of LiFePO₄ cathodes. For example, such efforts include increasing conductivity and accelerating the diffusion rate of Li⁺ ions through porous carbon and carbon coating layers. Such developments have used the coating of conducted materials on the surface of LiFePO₄ material (Zaghbi *et al.* 2013; Zhang *et al.* 2015; Yao *et al.* 2017; Wu 2018), doping transition metals ions (Wang *et al.* 2010; Chekannikov *et al.* 2018), and reducing the size of particles (Wang *et al.* 2014; Yang *et al.* 2014). The use of LiFePO₄ material has successfully improved the energy storage of lithium-ion batteries, which increased power production by adding an external carbon source (Arias-Thode *et al.* 2013). Chitin, an organic material derived from raw shrimp shell, goes through a typical reaction without the use of a catalyst or oxidant. In a typical reaction, 100 mg of chitin (4 mmol of carbon), 5 mL of 2 M NaOH, and a stirrer bar were loaded into the autoclave (Gao *et al.* 2016). The most available source of chitin and a major source is crustaceans, which are processed into chitin and chitosan. Chitosan after blending with a solid polymer electrolyte, plasticized with various weight percentages of polyethylene glycol (PEG) and LCIO₂ have been successfully prepared by a solution-casting method. This preparation can be used effectively as a promising material for the production of solid-state lithium ion batteries (Leo Edward *et al.* 2021).

This study assessed the modification of carbon produced from chitin (obtained from shrimp shells) for the carbon composite electrode. The carbon comprises small crystallites of electrode material with a uniform carbon coating that can improve the electrochemical activation of LiFePO₄ batteries. The study focuses on comparing the physical and electrochemical performances of polymer batteries using pure LiFePO₄ based on chitin-derived carbon coated on LiFePO₄, which comprised of a modified electrochemical activation process.

EXPERIMENTAL

Preparation of LiFePO₄ Material

The first step was the preparation of the chitin produced from the shrimp shells (Suratthani Province, Thailand), which were washed and cleaned before being processed into chitin. The samples were then sun-dried for 2 to 3 days before being completely dried in an oven at around 60 °C and being ground. Following that, 10 g of shrimp shell powder was mixed with 20 mL of acetone (Anantanara Co., Ltd., Thailand). Afterwards, 200 mL of hydrochloric acid (37% HCl; RCL Labscan, Thailand) was gradually added, and stirred in a flask that was kept in a tank of ice until the mixture was completely dissolved, which was then kept at 4 °C for 24 h. After 24 h, the substrate mixture was filtered through 2 to 3

layers of cheesecloth and added to 600 mL of a 50% ethanol solution (RCL Labscan, Thailand) with continuous stirring until precipitation, after which the top layer of the water was drained. Deionized water was then added in the same amount as the drained water, after which the pH balance was measured at 7.0. The substrate mixture was then centrifuged at 5,000 rpm for 10 min, steamed in an autoclave at 120 °C for 15 min, and stored at 10 °C.

The second step was to prepare the $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ precursor, which was done in a flask with iron (III) oxide (Fe_2O_3 ; Sigma Aldrich, Japan) powder and phosphoric acid (H_3PO_4 ; Sigma Aldrich, Japan) solution (85%), mixed with deionized water (DW), with the Fe/P/DW ratio being 2 g: 1.8 mL: 2.5 mL (Jiang *et al.* 2020). The mixtures were then transferred to a horizontal ball mill for 9 h, heated at 90 °C for 5 h to form a suspension, and then cooled to room temperature in the current study. In the final step, the $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ precursor was mixed with lithium carbonate (Li_2CO_3 ; Sigma Aldrich, Tokyo, Japan), chitin, and DW in the following proportions: 1 g: 0.485 g: 0.1 g: 32 mL (Ying *et al.* 2006) at room temperature. After that, the mixture was placed in an ultrasonic bath for 30 min. The mixed slurries were then oven-dried for 24 h at 85 °C. The mixture was then sintered at 650 °C in a tube furnace for 10 h with an argon flow of 3 °C/min to obtain the LiFePO_4 material shown in Fig. 1.

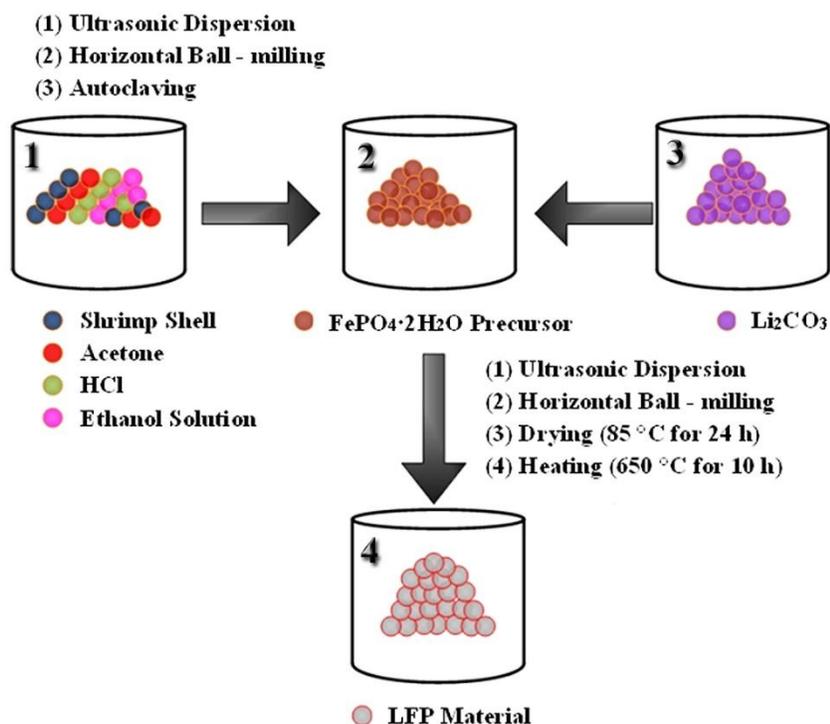


Fig. 1. Schematic illustration showing the preparation of LiFePO_4 material

Characterization of LiFePO_4 material

The phase identification of the LiFePO_4 material was carried out using X-ray diffraction (XRD; PANalytical Empyrean, Netherlands). The morphology and energy dispersive X-ray (EDX analysis) of the LiFePO_4 material were observed by scanning electron microscopy (SEM) with Quanta 400 (Thermo Fisher Scientific Quanta, Czech Republic). The specific surface areas were estimated using the multipoint BET

(Brunauer–Emmett–Teller, BET) model (Micromeritics equipment ASAP2460, USA), determining 11 closely spaced points in the relative pressure (P/P_0) range from 0.05 to 0.35. Prior to testing, samples (based on 50 to 200 mg in the form of powder) were degassed for 1 h at 30 °C under vacuum conditions to remove weakly adsorbed species.

Electrochemical measurements

For preparing the cathode, the LiFePO_4 material, carbon from chitin, and polyvinylidene fluoride (PVDF; Sigma Aldrich, Japan) were mixed at a ratio of 80:10:10 by weight. This mixture was mixed in a viscous slurry using N-methyl-2-pyrrolidone (NMP; Sigma Aldrich, Japan). The mixture was covered with aluminum foil and dried in a vacuum at 100 °C for 5 h. The composition was dried and formed into a film, which was loaded at a level of approximately 4.8 mg/cm² and used as the cathode. Meanwhile, copper plates were used as the current collector, reference electrode, and LiFePO_4 cathode material as the cathode. The electrolyte consisted of a solution of 1 mol/L LiPF_6 in ethylene carbon (EC)/dimethyl carbonate (DMC) (1:1 w/w) (Sigma Aldrich, Japan). The nano-power carbon (Sigma Aldrich, Japan) coated copper foil was used for the anode side.

The measurements of the battery cells were taken using an Autolab electrochemical impedance spectroscopy (Metrohm, PGSTAT302N, USA) as potentiostatic charge and discharge between 1.2 to 3.3 V with a scan rate of 0.1 to 0.5 V s⁻¹ at room temperature. Cyclic voltammetry (CV) was also tested. An electrochemical impedance spectrometer (EIS) was used to characterize samples using Autolab electrochemical impedance spectroscopy by adjusting the amplitude signal at 5 mV and a frequency range of 0.01 Hz to 100 kHz.

RESULTS AND DISCUSSION

Figure 2 shows the XRD patterns of LiFePO_4 synthesized with carbon produced from chitin. The XRD patterns of the sample revealed a highly crystalline stoichiometric LiFePO_4 phase in which 90% of major peaks were matched by the LiFePO_4 standard.

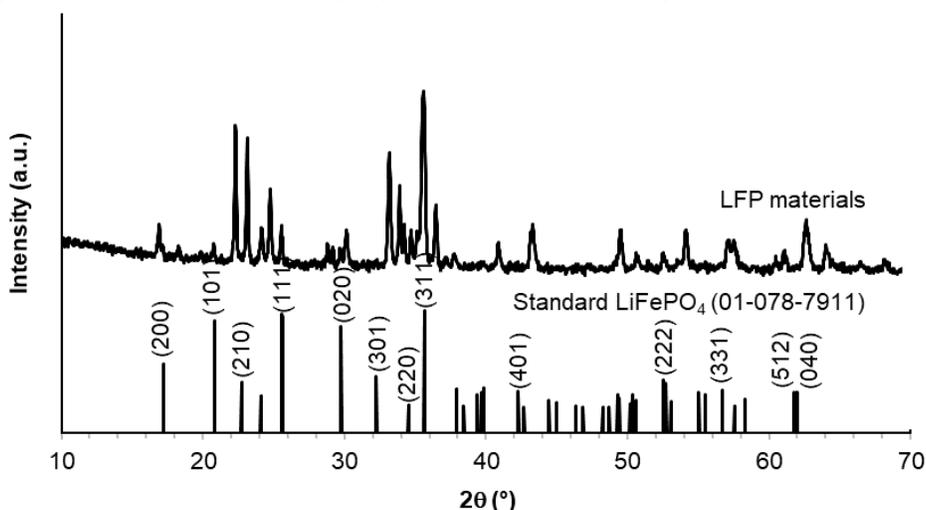


Fig. 2. XRD spectra of LiFePO_4 coated carbon (LiFePO_4/C) produced from chitin

The major phase of synthesized composite was confirmed with the Inorganic Crystal Structure Database (ICSD) file (No. 01-078-7911, Crystal system: Orthorhombic, Pnma (62), $a = 10.3254 \text{ \AA}$, $b = 6.0035 \text{ \AA}$, $c = 4.6879 \text{ \AA}$) (Gao *et al.* 2014). The XRD patterns of LiFePO_4 indicated a chitin peak of carbon contains calcium, presumably in the form of CaCO_3 , sodium, and sulphur (joined together in Na_2S and its derivatives Na_2S_4 or Na_2S_5) (Conder *et al.* 2019). This LiFePO_4 coated carbon composite was assessed for carbon element content with the EDX technique shown in Fig. 4.

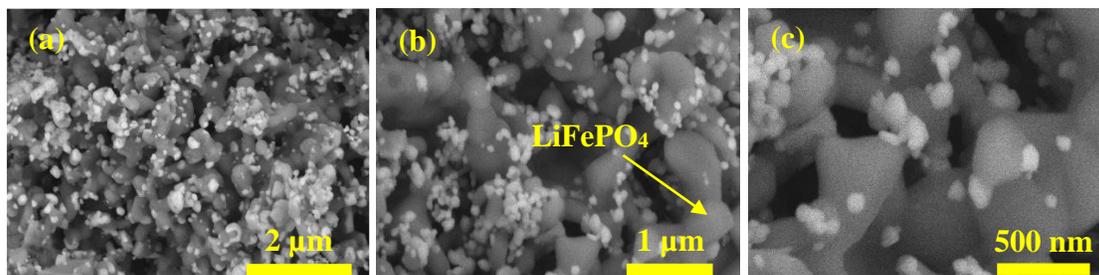


Fig. 3. A SEM micrograph of LiFePO_4 with carbon from chitin at (a) scale bar: $2 \mu\text{m}$, (b) scale bar: $1 \mu\text{m}$, and (c) scale bar: 500 nm

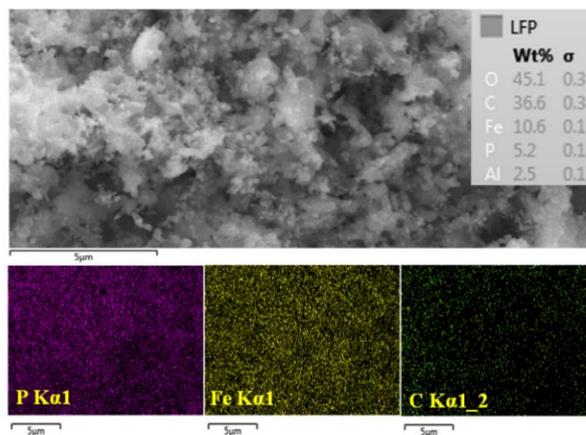


Fig. 4. EDX map of LiFePO_4/C composite; homogenous distribution of P, Fe, and C related to the presence of LiFePO_4 composite

Figure 3(a) shows SEM images of the LiFePO_4/C composite with C from chitin, indicating the high magnification of the coating. The LiFePO_4/C composite showed uniform particle size distribution as well as small grain sizes of approximately 0.5 to $1.0 \mu\text{m}$. This result was attributed to the carbon coating on the surface. The C-coating was homogeneously deposited on LiFePO_4 composite. Conductive carbon can be co-deposited with LiFePO_4 , which enhances the electrical conductivity of olivine-type LiFePO_4 thin films (Lu *et al.* 2008). Figure 3(b) shows a high magnification SEM image demonstrating both LiFePO_4 particles and carbon particles. The carbon particles can be found harmoniously mixed in the LiFePO_4/C composite. The particle aggregation was indicated by the particle size distribution measurement. Figure 3(c) shows a high magnification image based on the nano-size, indicating carbon particles with nano-particles. The sintering was confirmed to occur during the calcination process on the surface of the plates (Lyczko

et al. 2012). The particle aggregation based on elements of LiFePO_4/C can be revealed by colour, as shown in Fig. 4.

Figure 4 shows an EDX map of LiFePO_4 composite with carbon particles from chitin. The elemental contents of 5.20 wt% phosphorus (P) and 10.6 wt% iron (Fe) were mainly obtained from the LiFePO_4 composite. The content of 36.6 wt% carbon (C) was revealed from the carbon particles prepared from chitin, while 52.4 wt% consisted of other elements combined between Li and O. Additionally, the EDX map and SEM image (Fig. 3) certainly exhibited the highly homogenous composite of LiFePO_4/C . The LiFePO_4/C composite with co-deposited carbon showed homogeneous distribution throughout the LiFePO_4/C films. It was found that 2 mol% carbon was the optimized amount for the highest capacity (Lu *et al.* 2008). The mechanical activation operation is reported to be particularly efficient for synthesizing small particles with homogenous morphology (Kim *et al.* 2019).

Table 1. Surface Area and Pore Size of LiFePO_4/C

Sample	Surface Area (m^2/g)	Pore Size (\AA)	
		Adsorption average pore diameter	Desorption average pore diameter
LiFePO_4/C	4.47 m^2/g	157	169

The LiFePO_4 composites with carbon particle (LiFePO_4/C) crystals are mainly composed of smaller micro-crystals that are assembled in an orthorhombic structure, as shown in Fig. 2. Brunauer–Emmett–Teller (BET) analysis is shown in Table 1. The carbon coating of the samples (LiFePO_4/C) exhibited 4.47 m^2/g surface area and 157 to 169 \AA pore size. (Paolella *et al.* (2016) revealed 4.20 m^2/g surface area of the LiFePO_4/C with added Ca composite for an increased surface area.

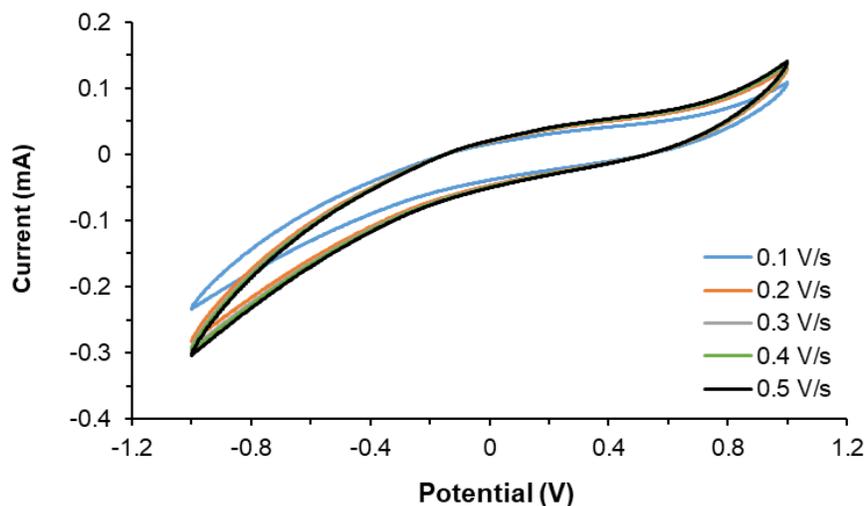


Fig. 5. Cyclic voltammetry of LiFePO_4/C cell curves at different scan rates

Cyclic voltammetry (CV) studies revealed the effect of carbon from chitin on the electrochemical properties of LiFePO_4 using a scanning rate of 0.1 to 0.5 V/s, as shown in Fig. 5. When the scanning rate was increased, the starting point of the cyclic voltammetry curve changed slightly, indicating that carbon can activate the stable cycling performance and that CV has no pseudo capacitance (Jiang and Xie 2019). The carbon from chitin for a

cathode composite had stable electrochemical cycling properties. The CV of LiFePO₄/C from chitin composites showed a highly symmetrical and sharper shape of the anodic/cathodic peaks, which indicates the better electrochemical process (Wang *et al.* 2010). The multi cycle from the first scan curve showed an irreversible cathodic peak at around 0.4 V and -1.0 V that can correspond to the generation of a solid electrolyte interphase (SEI) (Tao *et al.* 2020), and the appearance of well-indicated pair redox peaks indicates the redox activity of Fe²⁺/Fe³⁺ that is generated by lithium ion extraction/insertion in LiFePO₄ during the charge and discharge processes (Wu *et al.* 2016).

Figure 6 shows the Nyquist plot from the electrochemical impedance spectroscopy (EIS) of the LiFePO₄/carbon from chitin electrodes, which aimed to further study their electrochemical kinetics. The electrochemical activity of the LiFePO₄ cell 1.2 V was compared with cell 2.6 V and cell 3.1 V using the EIS technique. The EIS measurements were taken to explore the effect of carbon coating from chitin on the electrochemical performance of the LiFePO₄ cathode.

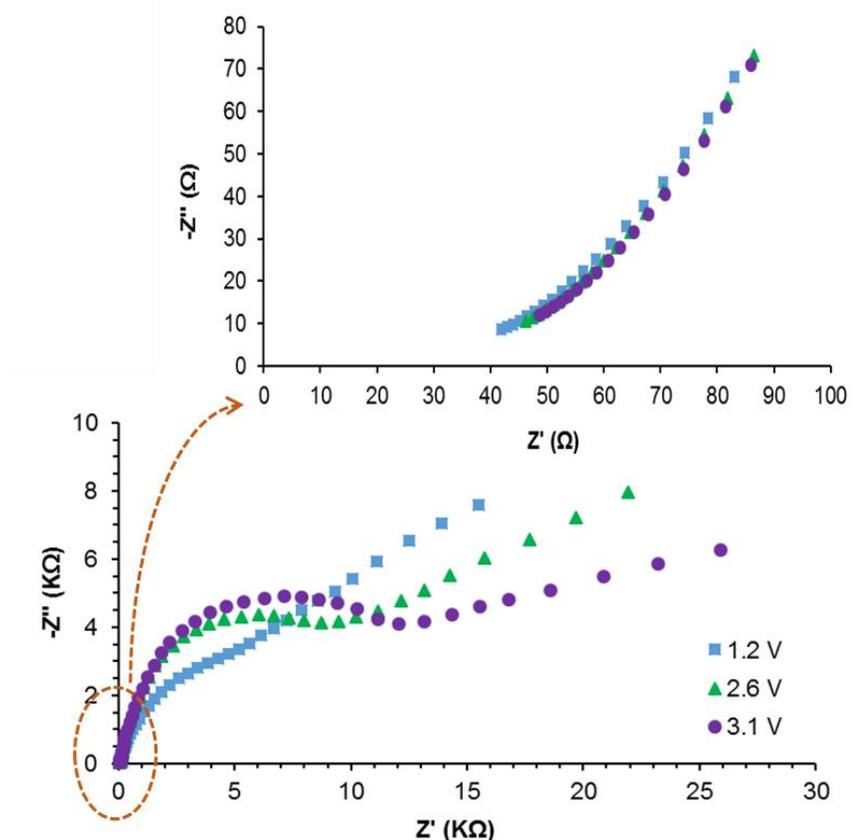


Fig. 6. Nyquist plot of electrochemical impedance spectra curves including cells at 1.2 V, 2.6 V, and 3.1 V

The charge transfer resistance represented the values for the cross point of the semicircle on the horizontal axes. The carbon from chitin was able to affect the first Nyquist plot (Z') at around 41 Ω , and the curves were moderately increased with higher voltage, while the end of the Nyquist plot was formed in a straight line that was slowly transformed to a semicircle with higher voltage. The straight line represents the Warburg impedance, which is associated with lithium-ion diffusion on the inside of LiFePO₄ particles.

Additionally, charge transfer resistance involves a close relationship between the composition and conductivity of the interface (Zhang *et al.* 2016; Sofyan *et al.* 2018).

In investigations using LiFePO₄ with carbon from chitin as a pumping solution, LiFePO₄ also showed an increase in current. For the LiFePO₄ with carbon from chitin, when operated at 1.2 V, the flow rate was increased to 80%, as shown in Fig. 7(a). This charge-discharge curve showed the high efficiency of the flow rate current. Electrochemical activation can be operated so that addition of Li⁺ to the pumping solution increases the ionic strength and flow rate of the pump (Baek *et al.* 2018). In a solution containing Li⁺, C may increase the high conductivity of carbon from chitin, which can result in faster charge and discharge (Wu 2018). Figure 7(b) shows the operation of the charge-discharge curves measured for LiFePO₄ with carbon from chitin when changing the active voltage at 1.9 V, 2.6 V, 3.1 V, and 3.4 V. The level of current is increased following the active voltage from 1.9 V to 4.3 V. When the cation was Li⁺, carbon exhibited the highest efficiency with the largest flow rate for the smallest current value. The grain size and crystallinity of the composite strongly influences the capacity. In terms of the capacity of organic carbon sources, LiFePO₄/C composite electrode prepared with a carbon source have a higher capacity (Chen *et al.* 2019).

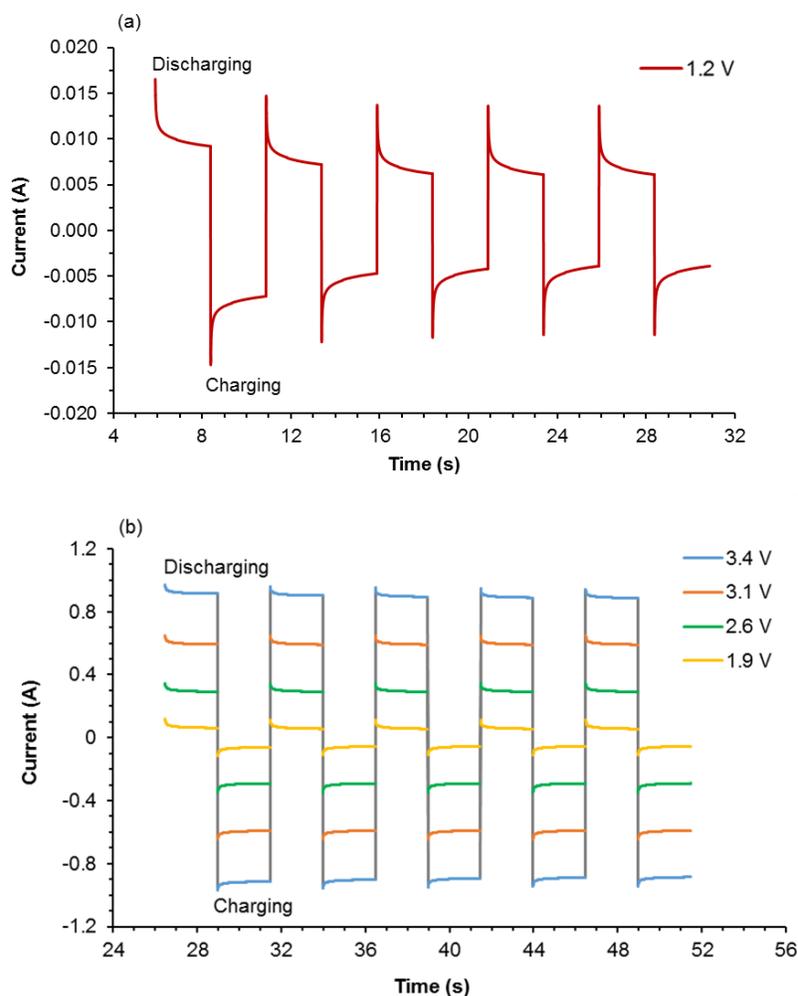


Fig. 7. (a) Charge and discharge current profiles of 1.2 V, and (b) comparison of charge and discharge current profiles between 1.9 V, 2.6 V, 3.1 V and 3.4 V

Figure 8(a) shows that the LiFePO_4/C cell has good rate capability with average charge-discharge capacities of 100 and -100 mAh/g once the voltage is operated at 3.4 V within 20 cycles. These results demonstrate the high cycling performance, capacity retention, and rate capability (Mohamed *et al.* 2014; Liu *et al.* 2015). Figure 8(b) shows the charge capacity of the LiFePO_4/C electrode *versus* the cycle number at a cycling specific capacity of 100 mAh/g; within 20 cycles, the capacity increases during the first 4 cycles. Thereafter, the trends were slightly decreased to 20 cycles (~ 100 mAh/g for cycle 20 charge capacity) with an improvement of 100% coulombic efficiency. The coulombic efficiency referred to the steady charge operation. The coulombic efficiency of these LiFePO_4/C electrodes subjected to galvanostatic charge/discharge was high with added amount of carbon in LiFePO_4 (Varzi *et al.* 2014).

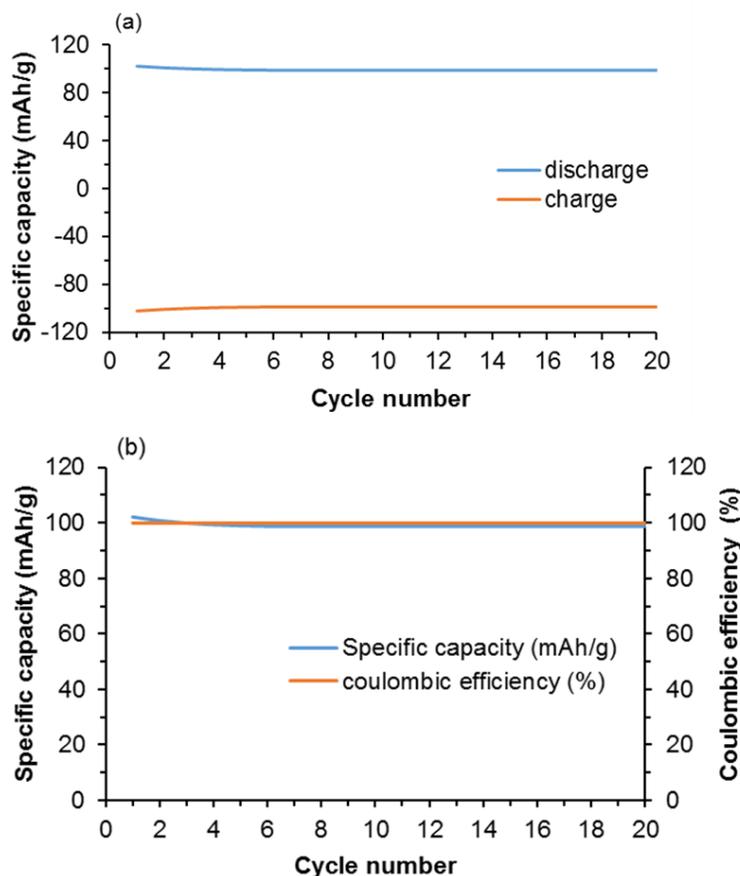


Fig. 8. (a) Charge and discharge profiles of 3.4 V; (b) cycling performance combined with coulombic efficiency of 3.4 V

Figure 9(a) shows the trends compared between the specific capacity and energy density at 20 cycles. The LiFePO_4/C electrode was revealed to have good rate capability with average charge capacities of 100 mAh/g, once the voltage was operated at 3.4 V, while the average energy density over a period of 20 cycles for LiFePO_4/C electrodes was 336 Wh/kg (maximum ~ 350 Wh/kg). The trends of specific capacity and energy density were similarly conducted; the trends were higher at 1 to 4 cycles and then gently were reduced to a straight line until 20 cycles. This manner of trend for energy density can occur in LiFePO_4 using carbon fibre-reinforced polymer (Moyer *et al.* 2020). Figure 9(b) shows the

trends compared between the coulombic efficiency and energy density at 20 cycles. At 1 to 4 cycles, both trends were different in that the trend for energy density was gently arched. At 4 to 20 cycles, both trends were formed in a straight line. This characteristic of the energy density trend can be formed at a high level in the first cycle and gently decrease to a straight line. This activation is generated in LiFePO_4 applying reinforced carbon fibre (Moyer *et al.* 2020), while the coulombic efficiency of LiFePO_4/C composite referred to charge/discharge is very high with an added amount of carbon (Varzi *et al.* 2014). The cost of LiFePO_4 when compared between this investigation and the market (Alibaba.com) indicates that materials from the market are cheaper than those in this investigation, while the manufacturing production permits low cost fabrication. However, this study used materials from an organic composite (chitin), which conformed to environmental composition standards for LiFePO_4/C batteries, as shown in Table 2.

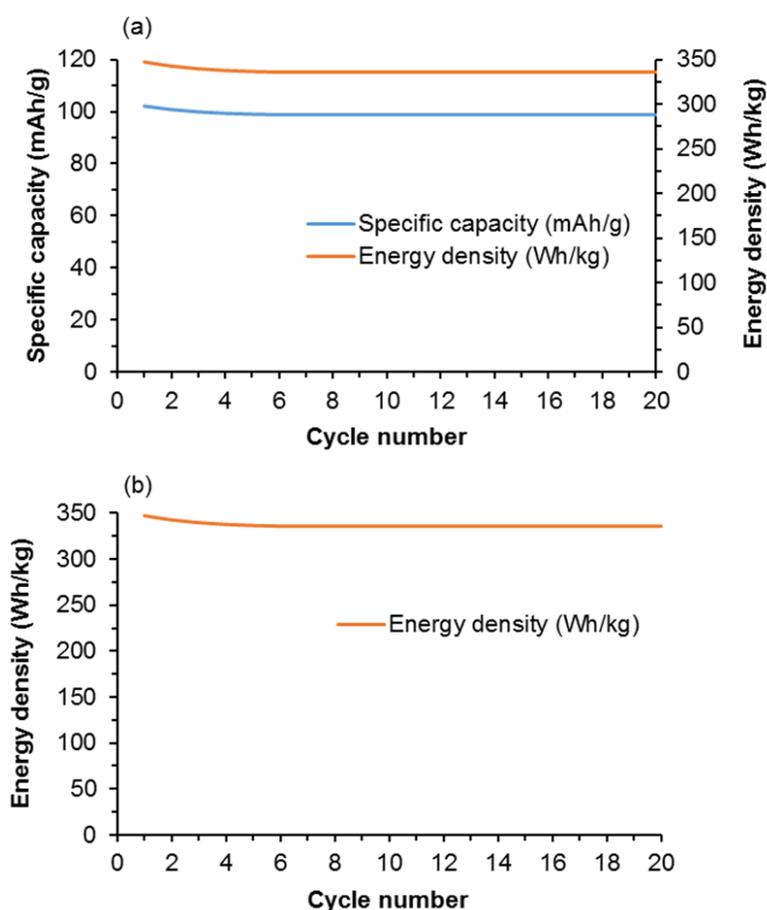


Fig. 9. (a) Cycling performance combined with energy density of 3.4 V; (b) energy density combined with coulombic efficiency of 3.4 V

Table 2. Comparison of LiFePO_4 Between this Investigation and the Market

Materials	Original Materials	Cost (USD)/g	Year
LiFePO_4/C	Website (Alibaba.com)	0.001-0.080	Feb. 2023
LiFePO_4/C	This investigation	0.132	Feb. 2023

CONCLUSIONS

1. This study used carbon (C) fabricated from chitin (produced from shrimp shell). The C formed small crystallites of the electrode composite with a uniform carbon coating that can improve the electrochemical activation of LiFePO₄ batteries.
2. The C produced from chitin revealed a C-elemental content of 36.6 wt%, which can be homogeneously mixed for LiFePO₄/C composition.
3. The electrochemical reaction of charge showed an increased current when LiFePO₄ used carbon from chitin; while operated at 1.2 V, the flow rate was increased 80%.
4. LiFePO₄ added with C from chitin cells exhibited good rate capability with average charge-discharge capacities of 100, and -100 mAh/g once the voltage operated at 3.4 V within 20 cycles.
5. LiFePO₄ added with C from chitin can generate average energy density of 336 Wh/kg (maximum ~350 Wh/kg) over a period of 20 cycles.

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