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Synthesis of LiFePO₄ in an Open-air Environment

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ABSTRACT

Among different efforts to increase the competitiveness of lithium-ion batteries (LIBs) in the energy storage marketplace, reducing the cost of production is a major effort by the LIB industry. This work proposes a synthesis method to decrease the production cost for LiFePO₄, by synthesizing the material through an open-air environment solid state reaction.

The lithium (Li)-ion battery is a member of the family of rechargeable batteries. In our approach, iron phosphate (FePO₄) powder is preheated to eliminate moisture. Once dried, the FePO₄ is mixed with lithium acetate (CH₃COOLi), and the mixture is heated in a tube furnace. The solid-state reaction is conducted in an open-air environment. In order to minimize the oxidation of the formed LiFePO₄, a modified tube reaction vessel is utilized during synthesis. X-ray Diffraction (XRD) and Energy Dispersive Spectroscopy (EDS) are used to characterize the crystal structure and chemical composition of the synthesized material. Furthermore, scanning electron microscopy (SEM) characterization shows the grain size of the formed LiFePO₄ to be in the range of 200 nm to 600 nm. Cycling testing of fabricated battery cells using the synthesized LiFePO₄ is done using an Arbin Tester.

INTRODUCTION

Rechargeable batteries. Its name is based on the fact that lithium ions move to the anode during discharge, and back to the cathode during charging. Lithium-ion batteries are widely used in applications ranging from personal electronics to large scale power systems. Li-ion batteries are suitable for portable devices because of their high-energy density, cost-competitiveness, and long cycle ability [1].

The typical structure of a half Li-ion coin cell consists of a lithium anode, a membrane, an electrolyte, and a cathode. A spacer, a spring, and a bottom case are connected with the anode. The coin cell is enclosed with a top case, and compressed. During discharge of the Li-ion battery the anode accepts lithium ions, and during charge the cathode intercalates the Li-ions. A complete charge followed by a discharge is referred to as a “cycle” [2].

LiFePO₄ has great potential in commercial applications for many reasons. Iron is abundant in nature [3], which makes LiFePO₄ cost competitive. It also has excellent thermal stability and cycle life [4]. Moreover, it has lower toxicity than traditional cathode materials such as LiCoO₂ and LiMn₂O₄ [5]. LiFePO₄ cell has a midpoint discharge potential of 3.45 V [6]. This value is relatively low when compared to LiCoO₂ and LiMn₂O₄ that have a midpoint voltage about 3.9 V and 4.05 V [5], respectively. However, LiFePO₄ exhibits a flat voltage profile, compared to a

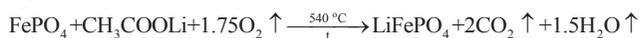
sloping voltage profile showed by LiCoO₂ and LiMn₂O₄. Thus, when both the voltage profile and midpoint discharge potential are considered together, LiFePO₄ cells have a higher specific energy than LiCoO₂ and LiMn₂O₄. Furthermore, LiFePO₄ cells have a longer cycle life indicating that they have very good capacity retention after hundreds of cycles [7]. This feature is significant for daily use electronic devices such as cell phones and laptops. An issue for LiFePO₄ is its low electrical and ionic conductivity [8]. LiFePO₄ has an olivine structure, and there are two types of building blocks in the crystal structure, PO₄ tetrahedral and FeO₆ octahedral. There is no continuous network of PO₄ and FeO₆ moieties, and one-dimensional channel is available for Li-ion transfer, leading to low conductivity. The value of the electrical conductivity for LiFePO₄ can be as low as 10⁻⁹ S/cm. In this case, a conductive additive such as carbon is applied to enhance electronic conductivity and facilitate electronic transport between the cathode and the current collector electrode.

Although the olivine like structure of LiFePO₄ is responsible for the low conductivity, it also provides robustness to the cell [9]. LiFePO₄ has the delithiated form (FePO₄), and this robust structure enhances the overcharging resiliency of LiFePO₄. Additionally, O atoms are strongly bounded to P in the PO₄ structure, which means O atoms have a lower tendency to be released into the electrolyte. This minimizes the possibility for the reaction between O atoms and the electrolyte under overcharge situation.

So far, the most widely used method in the industry to produce LiFePO₄ is solid-state method. However, this method requires long reaction time, higher reaction temperature, and the inert gas protection. These requirements all increase the cost of production. Thus, the goal of the proposed work is to develop an open-air high yield and cost effective synthesis process for making high quality LiFePO₄ cathode.

EXPERIMENT

In this research, LiFePO₄ is synthesized through an open air solid reaction method (Figure 1). Two precursors, FePO₄ and CH₃COOLi are applied for the synthesis of LiFePO₄ [10]. The reaction formula is



The FePO₄ is acquired via heating the hydrate FePO₄ powder at 300 °C for 2 hours. According to the reaction formula, FePO₄ and CH₃COOLi are mixed in 1:1 ratio by a Vortex Mixer. During the reaction, the mixed materials were heated in a tube furnace at 540 °C for a certain amount of time (t) in open air.

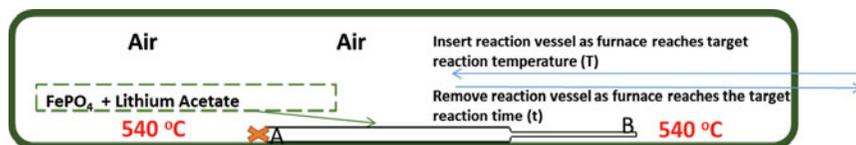


Figure 1. Experimental setup for synthesizing LiFePO₄ (the X in the figure indicates that the reaction vessel is sealed at that end).

In this work, LiFePO_4 material synthesized in 15, 18, 20, and 30 mins are investigated. XRD is used to provide insight into the crystallinity and production of LiFePO_4 . SEM is used to show the particle size of the synthesized LiFePO_4 . EDS is applied to detect the atomic percentage of each element in the synthesized LiFePO_4 . Battery cell with synthesized LiFePO_4 is assembled. Cycle test for the battery cell is conducted by an Arbin Tester.

RESULTS AND DISCUSSION

Figure 2. shows the XRD characterization results of LiFePO_4 synthesized at 540°C over 1) 15 min, 2) 18 min, 3) 20 min, and 4) 30 min. LiFePO_4 synthesized over 20 and 30 min show lower intensity on the (331), (121), and (222)/(402) peaks. On the other hand, they contain more peaks from Fe_2O_3 , denoted by the blue diamond. LiFePO_4 synthesized over 15 and 18 min, show stronger peaks on (331) and (121) direction, consistent with the presence of LiFePO_4 . All the matched peaks have been labeled on the figure. However, there are peaks from Fe_2O_3 in the XRD results for a reaction time of 15 and 18 min samples, indicative that some LiFePO_4 is oxidized during the reaction. Thus, the synthesis should be further optimized. It is noticed that the strongest peak is always the (331) peak independent of the reaction time. This is because both Fe_2O_3 and LiFePO_4 show the strongest peak at this angle [11]

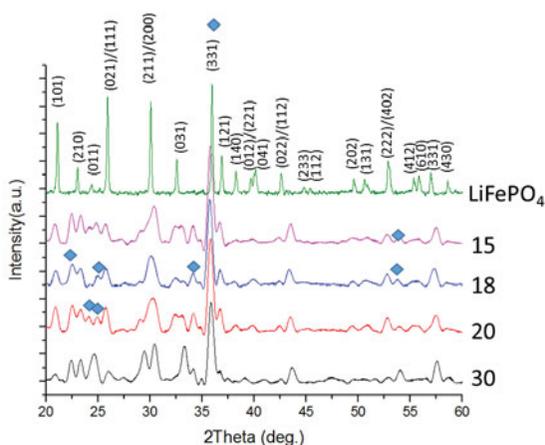


Figure 2. XRD patterns for the synthesized materials in an open-air environment over various reaction times: 15 min (purple), 18 min (blue), 20 min (red), and 30 min (black).

From the characterization results, we can observe that part of the formed LiFePO_4 is oxidized into the Fe_2O_3 during the synthesis reaction. The reaction also produces Li_3PO_4 as a byproduct material. Because Fe_2O_3 is not an active material for the cathode, it decreases the performance of

the LIBs. Thus, it is critical to minimize the oxidation of LiFePO_4 during synthesis. The reason why LiFePO_4 oxidizes is because in the open air environment the partial pressure of the O_2 is too high during the reaction. Although carrying out the synthesis in the open air simplifies the experimental set up and has the potential to significantly decrease the cost of synthesis, it requires some level of control on the amount of oxygen available during the reaction. Thus, a tube reaction vessel with a large gas intake (labeled as (A) in Figure 1) is used. The end (A) is also used to feed the precursors and then sealed before the reaction takes place. The small gas intake (labeled as (B) in Figure 1) is used as a self-regulating intake channel to control the amount of oxygen that participates during the synthesis reaction.

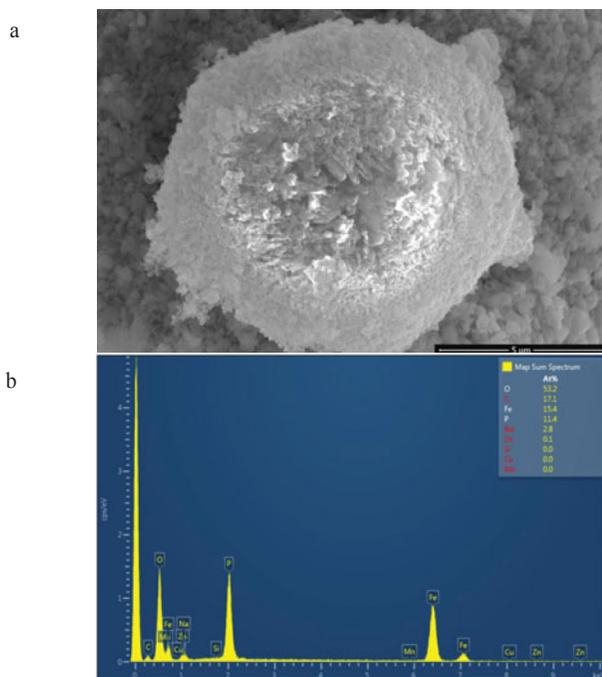


Figure 3. a) SEM, and b) EDS images for a synthesized LiFePO_4 with 18 min reaction time.

Figure 3a shows the SEM image of synthesized LiFePO_4 over a reaction time of 18 min at a magnification of 10,000 times. It is noticeable that in addition to smaller grains, large clusters of particles are also produced, as shown in the middle of the image. Figure 3b shows the EDS map sum spectrum result for Figure 3a. According to the spectrum, the synthesized LiFePO_4 with 18 min heating shows 15.4 At% of Fe and 11.4 At% of P. The discrepancy in At% between Fe and P is caused by the presence of Fe_2O_3 .

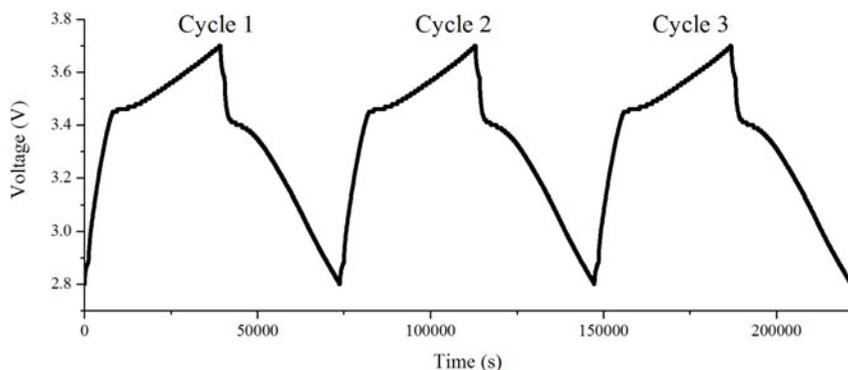


Figure 4. Cycling test for battery cells with LiFePO_4 synthesized in open-air environment over 18 mins.

Figure 4. is the cycling test results for a battery cell fabricated with LiFePO_4 synthesized in open-air environment over 18 mins. During the cycling test, the cell is charged and discharged between 3.7 V and 2.8 V. The current applied to battery cell is 2.5×10^{-6} A. Three full charge/discharge cycles are shown on the figure. The curve shows a cell with very short discharging time under this condition. Especially the discharge platform is short and is hard to observe in the figure. This shows that the presence of Fe_2O_3 does have a significant impact on the electrochemical performance of the cell. The yield of Fe_2O_3 decrease the amount of LiFePO_4 (active materials) in the cathode and thus decreases the capacity of the cell. It can even defunctionalize the battery cells. The quality of synthesized LiFePO_4 needs improvement and the synthesis method needs further optimization.

CONCLUSION

LiFePO_4 was successfully synthesized in open air environment in a short period of reaction time (18 min). This synthesis method has the advantage of a low equipment requirement (i.e. tube furnace). However, oxidization of the final product occurred during the reaction and the production amount of LiFePO_4 was decreased that caused an electrochemical performance loss for the battery cell. The next step for this research is to minimize the oxidation effect during reaction, via optimization of reaction temperature, time, reaction vessel design, and a better control on the amount of air that participates in the reaction.

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REFERENCES

1. M. Yoshio, R.J. Brodd, and A.Kozawa, *Lithium-Ion Batteries: Science and Technologies*, 1st ed. (Springer Science+Business Media, New York, 2009) p. 1-8.
2. W. Schalkwijk, and B. Scrosati, *Advances in lithium-ion batteries*, 1st ed. (Springer Science+Business Media, New York, 2002) p. 79-101.
3. P.H. Holloway, and P.N. Vaidyanatban, *Characterization of Metals and Alloys*, 2nd. (Momentum Press, New York, 2010) p. 4-6.
4. A. Yamada, S.C. Chung, and K. Hinokuma, *Journal of Electrochemical Society*, **148**, 3 (2001).
5. B. Scrosati, and J. Garche, *Journal of Power Sources*, 195 (2010).
6. D.Y.W. Yu, C. Fietzek, W. Weydanz, K. Donoue, T Inoue, H. Kurokawa, and S. Fujitania, *Journal of The Electrochemical Society*, **154**, 4 (2007).
7. H. Wu, C. Su, D. Shieh, M. Yang, and N. Wu, *Electrochemical and Solid-State Letters*, **9**, 12 (2006).
8. J. Li, W. Yao, S. Martin, and D.Vaknin, *Solid State Ionics*, 179 (2008).
9. X Yuan, H Liu, and J Zhang, *Lithium-ion batteries: advanced materials and technologies*, 1st. (CRC Press, Boca Raton, 2011)p. 51-97.
10. P.P. Prosini, M. Carewska, and Mauro Pasquali, *Solid State Ionics*, 286 (2016).
11. J. Chen, and J. Graetz, *Appl. Mater. Interfaces*, **3**, 5 (2011).