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Effects of Ionic Liquid to Water Ratio As a Composite Medium for Synthesis of $LiFePO_4$ for Battery

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ABSTRACT

$LiFePO_4$ is a highly researched cathode material that serves as an alternative material for traditional commercial lithium-ion batteries such as $LiCoO_2$. Currently, there are a number of different methods to synthesize $LiFePO_4$ including: hydrothermal, solid state, spray pyrolysis, and coprecipitation. Our proposed method has the potential to provide an ecologically friendly and economically competitive way to synthesize $LiFePO_4$ by utilizing ionic liquid and water, as a composite synthesis medium. The addition of water to ionic liquid can be beneficial as it can act as a mineralizer to bring insoluble precursors to form $LiFePO_4$ seed crystals. Furthermore, this method provides the possibility of recycling the ionic liquid for repeated synthesis processes. In this work, we study the effects of ionic liquid to water ratio on the crystallinity and morphology of the synthesized material. Our group was able to conclude a reaction medium utilizing a ratio of equal parts of 1-ethyl-3-methyl imidazolium trifluoromethane sulfonate (EMIM Otf) and water, or a slightly favored ionic liquid ratio, increases the efficacy of the synthesis route. Crystallinity and purity was determined by X-ray diffraction (XRD), scanning electron microscopy (SEM) was used to determine morphology and crystal sizes, and energy dispersion spectroscopy (EDX) was used for elemental analysis.

Keywords: energy, materials, battery, lithium-ion, storage, synthesis, green

1. INTRODUCTION

Lithium-ion batteries are chosen in part because of their desirable properties that classify them as secondary storage devices—they are rechargeable. Within the domain of lithium-ion batteries lies a plethora of cathode materials that are chosen based on their inherit properties. $LiCoO_2$ is chosen for applications that require a high discharge rate and high specific capacity such as in cellular devices and electronics. But in areas where safety concern is deemed a high priority, $LiCoO_2$ can be an issue [1]. $LiFePO_4$ has been studied as a safer alternative to $LiCoO_2$ for special use cases such as in grid storage [2]. In particular, $LiFePO_4$ has redeeming properties such as a long cycle life, a flat discharge curve and a higher tolerance for abuse [3]. Along with the material's excellent safety measures lies a low specific energy coupled with low material conductivity. In order to assuage these limiting factors, research areas in cation doping, carbon coating, and morphology manipulation have been explored [4].

By altering the process in which $LiFePO_4$ is synthesized, the material's morphology and crystallinity can be manipulated. Specifically for $LiFePO_4$, material scientists have sought to increase the surface area of $LiFePO_4$ crystals to allow large quantities of lithium ions to diffuse out of the crystal lattice [1,4]. In addition to this optimization, what is necessary is for the travel time for lithium ions to leave the crystal lattice to be decreased by modifying the diffusion

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distance [5]. In light of these phenomena, numerous synthesis methods have surfaced to tackle these issues. For example, hydrothermal synthesis utilizing water and a glycol medium was studied for morphology control [6]. What was found was that by optimizing the ethylene glycol to water ratio, and the types of precursors used different crystal morphologies were obtained. In another attempt, $LiFePO_4$ was synthesized with oleic acid, ethylene glycol and hexane to create unique $LiFePO_4$ nanoflowers [7]. Not only is morphology important for strong electrochemical results, but the synthesis process itself must be well-adapted to be scaled and utilized for industry. In light of this, Recham et. al. reported an alternative low-temperature synthesis method by applying ionic liquids as a synthesis medium [8]. Ionic liquids are known to be flexible in their physical properties by interchanging cation/anions pairs [9]. Moreover, room temperature ionic liquids (IL) are known to be thermally stable, have negligible volatility and can direct nucleation [citation needed]. As a result of the aforementioned synthesis methods and their benefits, we explore the possibility of a multi-solvent system that capitalizes on $FeSO_4 \bullet 7H_2O$ solubility in water and ionic liquid's nucleation directing properties.

2. METHODOLOGY

2.1 Experimental Set-up and Instrumentation

Table 1. Ratios that are tested at 260°C for 18 hours. IL and W represent ionic liquid and Millipore water, respectively.

Ratio (IL:W)	Volume
2:1	10 mL IL, 5 mL H_2O
1:1	7.5 mL IL, 7.5 mL H_2O
1:2	5 mL IL, 10 mL H_2O
3:0	15 mL IL

$FeSO_4 \bullet 7H_2O$ (Sigma Aldrich) and Li_3PO_4 (Sigma Aldrich) are first mixed together in Millipore water for one hour on a hot plate for one hour. Afterwards, EMIM Otf (Sigma Aldrich) is added and stirred on the hotplate again for one hour and then placed into a sonicating bath for 1 hour. During sonication, a cap is put over the vessel to avoid the loss or introduction of extra water from the bath. At the final step, the mixture is placed into a furnace with nitrogen flow and is ramped to 260 °C in 30 minutes and held at a constant temperature for 18 hours. After 18 hours, the system is allowed to cool down via ambient temperature from the environment.

For our analysis, crystal structure was analyzed by X-ray diffraction (Panalytical X'Pert) with Cu Kα radiation. SEM and EDS were done with a NovaNano SEM 450 to evaluate crystal morphology and elemental traces.

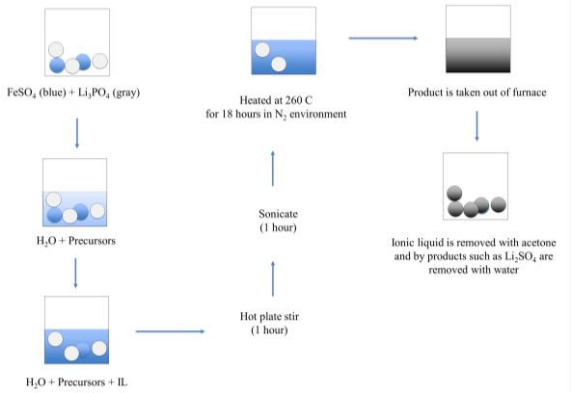

Figure 1. Schematics of the synthesis process for $LiFePO_4$.

3. RESULTS AND DISCUSSION

3.31 X-ray Diffraction

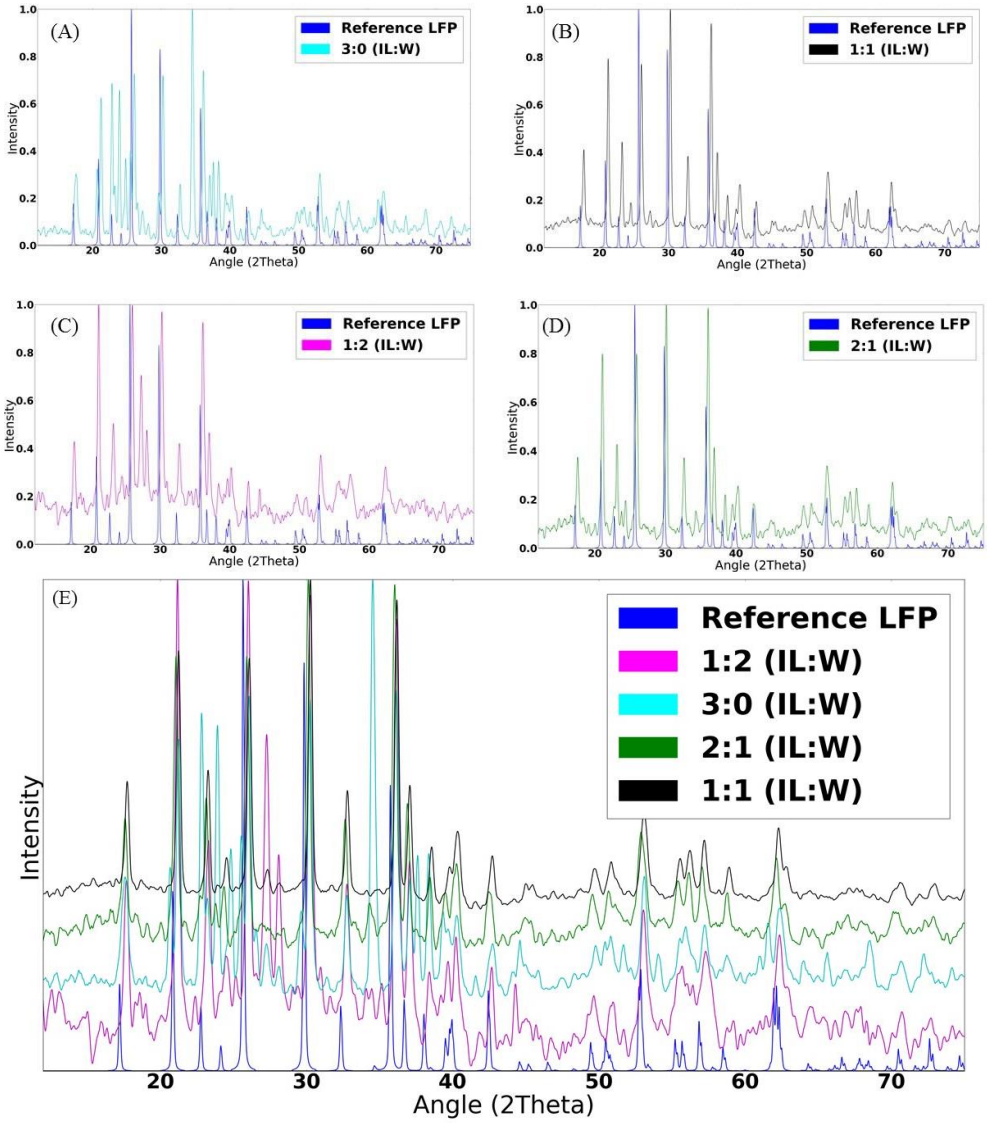

Figure 2. X-ray diffractograms for (A) 3:0 (B) 1:1 (C) 1:2 (D) 2:1 ratios and (E) a composite of all the ratios.

The crystal structure and composition of synthesized $LiFePO_4$ were determined by X-ray diffraction as seen in Figure 2. From these diffractograms, it is indicated that narrow peaks and relatively strong intensity demonstrate a relatively high crystallinity while broad peaks can represent low crystallinity material. Furthermore, from the peak placements seen in each diffractogram, all of the ratios were able to synthesize $LiFePO_4$. Although each ratio was able to yield $LiFePO_4$, it

is seen that all the ratios contain uncorrelated peaks with $LiFePO_4$ seen in the range of $2\theta = 20\text{-}40°$. The ratio 3:0 shows to perform the worst as indicated by a strong uncorrelated peak in the range of $2\theta = 30\text{-}40°$ in Figure 2(D). In contrast, a ratio of 1:1 has the strongest correlation with referenced $LiFePO_4$ as most peaks align with referenced $LiFePO_4$.In addition, the aforementioned peaks that do not correlate with $LiFePO_4$ are seen to have the lowest intensity in a ratio of 1:1. In comparison to one another, the ratios indicate that the highest efficacy from highest to least are: 1:1, 2:1, 1:2, 3:0.

3.2 SEM and EDX

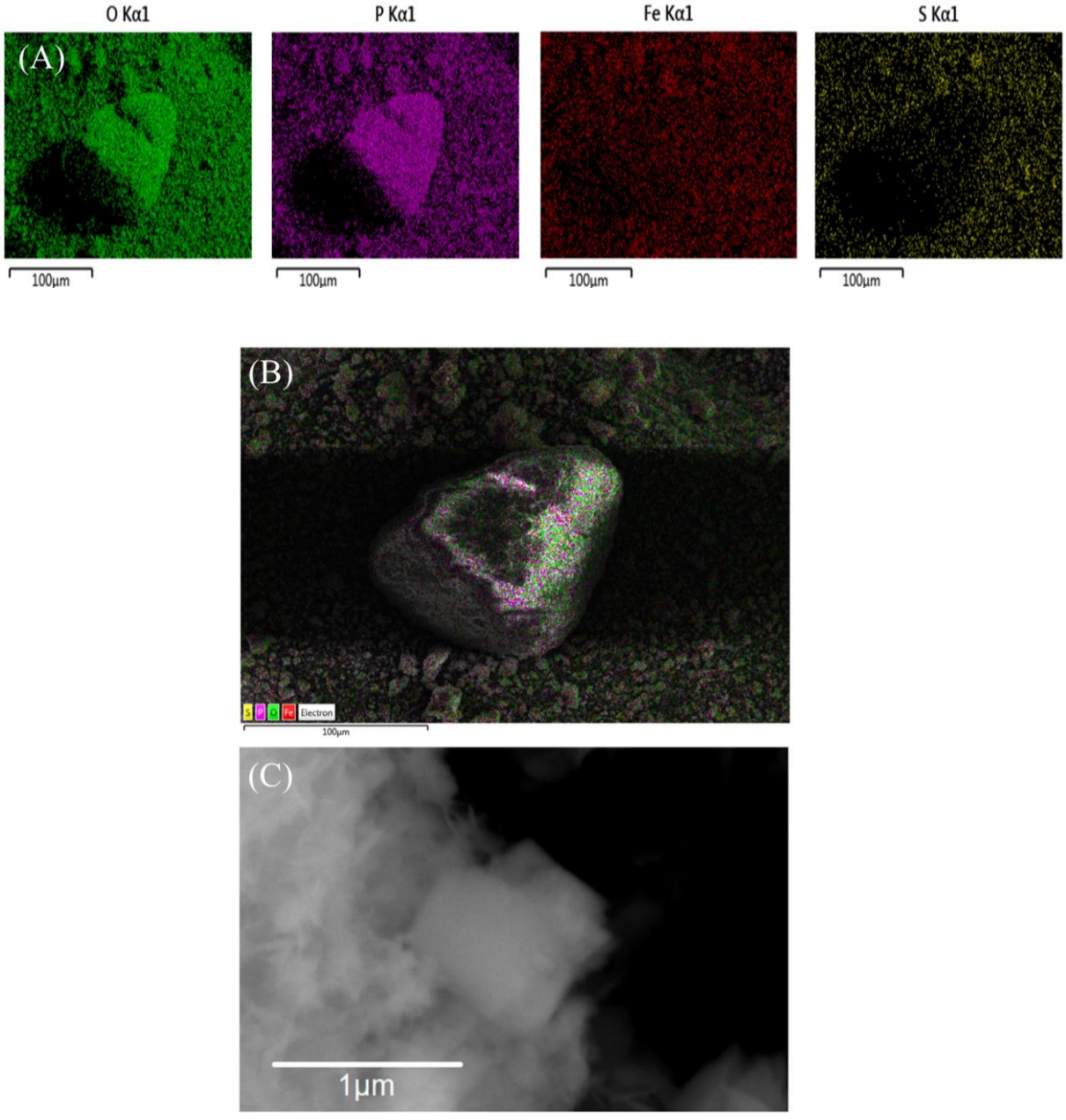

Figure 3. (A) Individual EDX maps, (B) overall map for trace elements and (C) SEM of material from a 1:1 ratio synthesis.

From the EDX results in Figure 3(A)A, traces of sulfur are found in the bulk material that was synthesized by a 1:1 ratio. This trace of sulfur can be hypothesized to originate from Li_2SO_4, as a byproduct of the synthesis method. This is given from the chemical reaction equation: $Li_3PO_4 + FeSO_4 \rightarrow LiFePO_4 + 2Li^+ + SO_4^-$.[ref] More importantly, the large particle that is shown in Figure 3(B) can be attributed to unreacted Li_3PO_4. This is concluded from the oxygen and phosphorous maps indicating a prominent outline of the particle; however it is then seen to disappear on the iron map. Figure 3(C) indicates the produced $LiFePO_4$ morphology of stacked nanoplates as seen in the center. Next to the stacked nanoplates are needle-like structures that are hypothesized to be attributed from impurities that have not been washed out such as Li_2SO_4.

4. CONCLUSION

An ionic liquid to water ratio study was done on a proposed composite synthesis medium for $LiFePO_4$. Stacked alternating nanoplates were synthesized with a 1:1 ratio at 260 °C for 18 hours with impurities. The ratio between the ionic liquid and water plays a crucial role in determining the purity of the synthesized product. For future works, traces of Li_2SO_4 will be removed, unreacted precursors will be filtered out, and a heat treatment will be applied allowing synthesized material to be tested electrochemically.

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