



Preliminary Study of LiCoPO_4 cathode material synthesis for LiCoPO_4 /Graphite Cell

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ABSTRACT: Nowadays, the race toward a high-performance Li-ion battery discovery for energy storage has become an interesting technological challenge. New or improved Li-ion battery cathodes have been developed relentlessly in this decade. LiCoPO_4 (LCP) is a cathode material that allows a battery to operate at a high voltage which resulted in a high energy density battery. The presence of a strong P-O bond adds a thermal stability feature to LIB cells. In this study, LiCoPO_4 material was prepared by precipitation of $\text{Co}_3(\text{PO}_4)_2$ (CP) followed by high-temperature Li insertion. H_3PO_4 was used as the phosphate source. The crystallization or precipitation of CP can only be achieved under mild pH conditions, which can be controlled using sodium hydroxide. XRD, SEM, and FTIR analysis were used to characterize the final product. The as-obtained LCP was applied as cathode material while graphite was used as the counter anode. The cell can deliver a charge-discharge capacity at a voltage of 2.0-4.95 V. This preliminary can be a groundwork toward the commercialization of LCP-based Li-ion batteries for high duty applications.

Keywords: LiCoPO_4 , cathode, high-voltage, Batteries, Energy Storage.

1. Introduction

The emerging energy storage technology such as Li-ion batteries allows the rapid development of advanced vehicles and renewable energy. Current efforts to improve the performance of Li-ion batteries have aimed to widen its application in several areas, specifically high duty applications. Nowadays, the main challenge in the development of high-performance energy storage systems is to provide batteries with high energy density with high

safety aspects. Currently, LiFePO_4 is considered the safest Li-ion cell . It utilizes LiFePO_4 and graphite or $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) as the cathode and the anode material. However, the cells suffer from low energy density and low ionic-electronic conductivity[2].

LiCoPO_4 is isostructural to LiFePO_4 . It has an olivine-type structure with considerably good safety aspects and thermal stability due to a strong P-O bond[5]. Theoretically, it has a similar specific coulombic capacity

to LiFePO_4 but a significantly higher operating voltage of >4.8 V. This can result in a high energy density Li-ion battery. In comparison to LiCoO_2 with Co as the sole transitional metal, LiCoPO_4 has lower Co content and higher safety. Therefore, the overall production cost is far less expensive. To improve the overall production cost of material, the simplicity of material processing is highly necessary[12].

There are several techniques to prepare LiCoPO_4 such as solid-state reaction, hydrothermal, molten salt, solvothermal, sol-gel, spray pyrolysis, and precipitation. The precipitation route is the simplest techniques compare to other solution route methods. It does not require sophisticated apparatus, the starting material is not limited to decomposable salts such as nitrates and acetates, and delivers a homogenous particle with narrow size distribution[7,10].

In this paper, LiCoPO_4 is synthesized via a precipitation process to obtain the precursor as cobalt phosphate or $\text{Co}_3(\text{PO}_4)_2$. The solubility product constant of $\text{Co}_3(\text{PO}_4)_2$ is $\sim 2 \times 10^{-35}$ which shows that it is easy to be precipitated. The LiCoPO_4 can be obtained via solid-state reaction between the precursor, lithium, and phosphate sources at high temperatures. The as-prepared powders are analyzed thoroughly. In the end, this study provides the groundwork for the development of LiCoPO_4 material on at a large scale.

2. Materials and Methods

2.1. Synthesis of LiCoPO_4

Cobalt sulfate heptahydrate was used as a source of Co. 1 mole of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved in demineralized water to obtain 1 M CoSO_4 in a beaker glass. Separately, 1 mole of H_3PO_4 was dissolved to obtain a 1 M solution. The cobalt sulfate solution was continuously stirred at a speed of 300 rpm using a magnetic stirrer. The phosphoric acid solution was transferred into a cobalt sulfate solution containing a beaker. 1 mole

of NaOH was dissolved in demineralized water, and reacted with cobalt phosphate solution until the pH number 4 and 6 to obtain $\text{Co}_3(\text{PO}_4)_2$ powder samples labelled as $\text{Co}_3(\text{PO}_4)_2$ A and $\text{Co}_3(\text{PO}_4)_2$ B, respectively. The solution is stirred for 60 minutes and the formed precipitates are allowed to settle. The precipitates were filtered and washed for three times using deionized water to eliminate dissolved impurities. The as obtained precipitate was dried in an oven for a night. Lithium carbonate (Li_2CO_3) is added to dry cobalt phosphate powders and mixed with mortar and pestle, then sintered in a box furnace at 600°C for 4 hours under atmospheric air.

2.2. Characterization of LiCoPO_4

The cobalt phosphate precipitates and LiCoPO_4 was characterized using X-ray diffractometer (MD-10 mini diffractometer) at diffraction angle of $17 < \theta < 71^\circ$ and $\text{CuK}\alpha$ wavelength of 1.5418 \AA , Fourier's transformed infra-red (FTIR) spectroscopy (Shimadzu, Japan). The morphology of the cobalt phosphate and LiCoPO_4 powders is investigated by scanning electron microscope (SEM JEOL Japan).

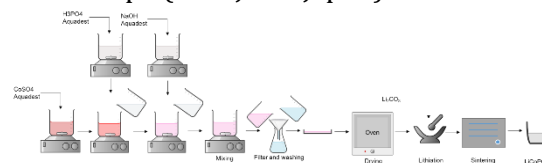
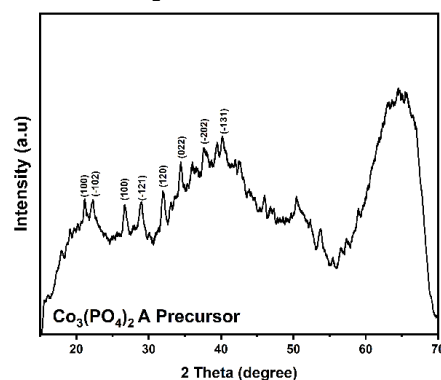


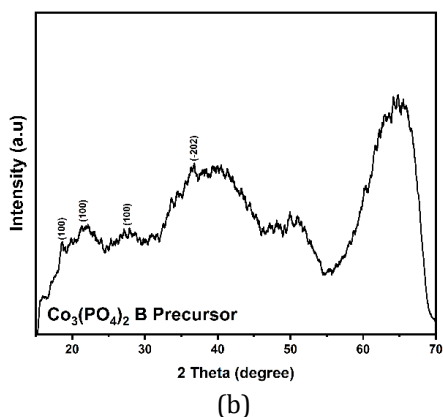
Figure 1. Synthesis of LiCoPO_4 powder

3. Result and Discussion

3.1 Cobalt Phosphate Characterization

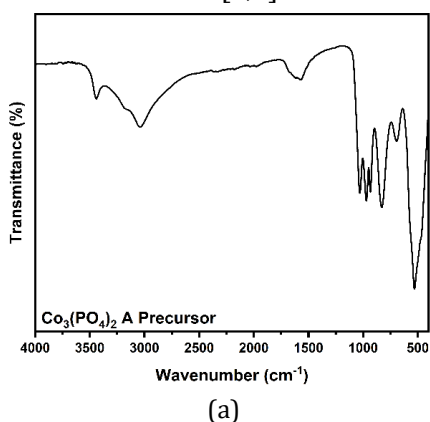


(a)

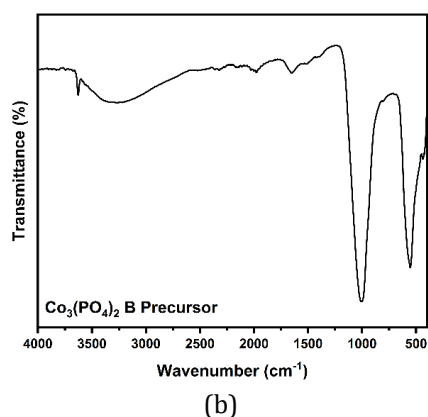


(b)
Figure 2. X-ray diffraction spectra of cobalt phosphate powders

Figure 2a shows the XRD pattern of the $\text{Co}_3(\text{PO}_4)_2$ A precursor and Figure 2b shows the XRD pattern of the $\text{Co}_3(\text{PO}_4)_2$ B precursor through the precipitation pathway. Cobalt phosphate precursor material has peaks in the diffraction pattern according to the diffraction peaks of $\text{Co}_3(\text{PO}_4)_2$ JCPDS 70-1795. However, in cobalt phosphate with a pH number of 6, there are only a few peaks that similar with JCPDS. This indicates that the cobalt phosphate A precursor material has been formed, the peak in the narrow diffraction pattern indicates that the crystal size formed is larger and the pure phase. Deep analysis in order to understand the precipitation reaction is performed by the FTIR characterization[3,4].

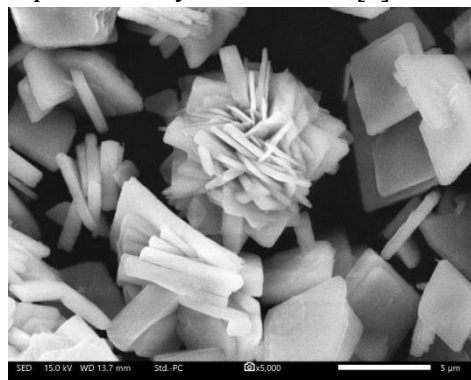


(a)



(b)
Figure 3. FTIR spectra of cobalt phosphate powders

FTIR analysis was used to determine the groups formed on $\text{Co}_3(\text{PO}_4)_2$ particles. Figure 3 show FTIR spectra from $\text{Co}_3(\text{PO}_4)_2$ A particles, H_2O bonds appeared in the antisymmetric stretching mode range of $3810 - 3095 \text{ cm}^{-1}$. The vibrational band at 689 cm^{-1} is ascribed to the $\text{V}_4(\text{F}_2)\text{PO}_4^{3-}$ mode of the phosphate (PO_4) group. The broad characteristic peaks at 1017 and 1400 cm^{-1} are attributed to the survival of the $\text{P}=\text{O}$ stretching vibration in PO_4^{3-} and the $\text{P}-\text{O}-\text{P}$ stretching vibration in the HPO_4^{2-} group, respectively. However, in $\text{Co}_3(\text{PO}_4)_2$ B material, there is no $\text{P}-\text{O}-\text{P}$ stretching vibration. To ensure that the material that has been formed, the SEM-EDX characterization have been carried out. This shows that in higher pH level, the cobalt is precipitated in hydroxide form[6].



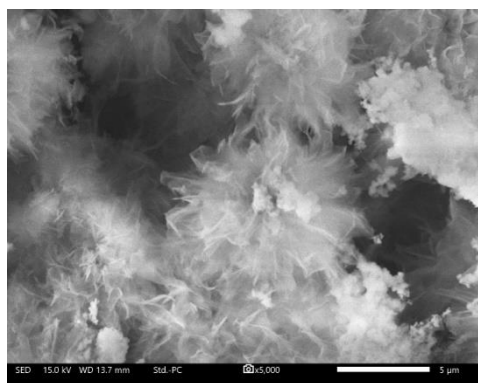


Figure 4. SEM images and EDX results of cobalt phosphate powder with pH 4 (up) and pH 6 (bottom)

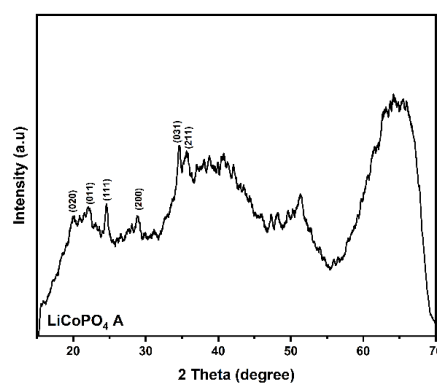
Figure 4 shows an electron microscope scan (SEM) image of a cobalt phosphate powder sample. The morphological shape between the 2 samples is different from cobalt phosphate with a pH number 4 is in the form of nanoflakes particle. Compared to those with a pH number of 6, have a flower like morphological shape. but have almost the same particle size of about 5 microns. Cobalt phosphate A has a higher purity as evidenced by the EDX characterization in Table 1 compared with cobalt phosphate B which has some impurities could be caused by the addition of NaOH. It is predicted that in the cobalt phosphate sample processed at pH 6 there is still unreacted cobalt sulfate, and contain sodium cobalt phosphate mixture[8].

Table 1. EDX Analysis of $\text{Co}_3(\text{PO}_4)_2$ at pH 4 and 6

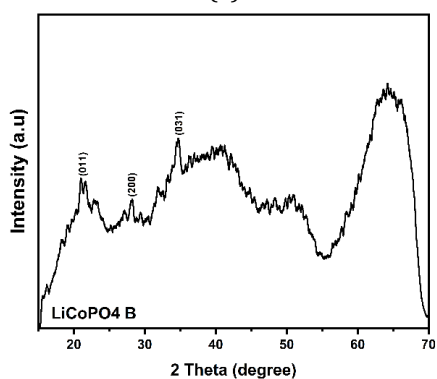
$\text{Co}_3(\text{PO}_4)_2$ pH 4			$\text{Co}_3(\text{PO}_4)_2$ pH 6		
Element	Mass %	Atom %	Element	Mass %	Atom %
O	56.58 ±0.95	79.35 ±1.33	C	4.72 ±0.35	9.03 ±0.66
P	12.00 ±0.41	8.69 ±0.30	O	40.43 ±0.91	58.06 ±1.30
			Na	11.20 ±0.56	11.20 ±0.56

Co	31.42 ±1.53	11.96 ±0.58	P	9.78 ±0.38	7.26 ±0.28
			S	3.83 ±0.24	2.75 ±0.17
Total	100.00	100.00	Co	30.04 ±1.52	11.71 ±0.59
			Total	100.00	100.00

3.2 LiCoPO_4 Characterization



(a)

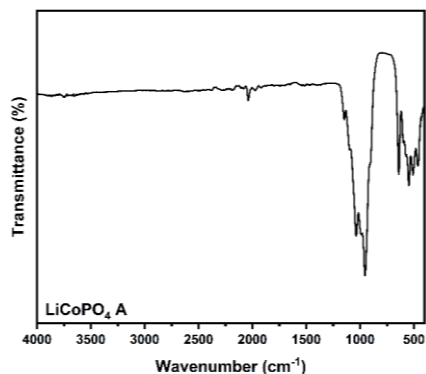


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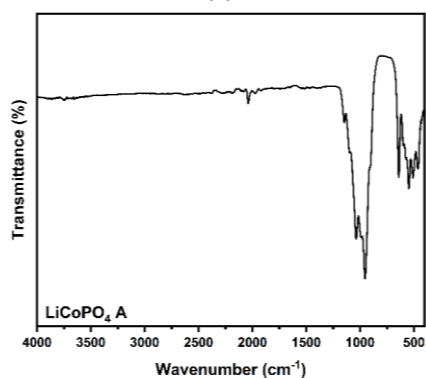
Figure 5. X-ray diffraction spectra of LiCoPO_4 powder

Figure 5a shows the XRD pattern of the LiCoPO_4 A and Figure 5b shows the XRD pattern of the LiCoPO_4 B through the precipitation pathway. LiCoPO_4 material has peaks in the diffraction pattern according to the diffraction peaks of LiCoPO_4 JCPDS 00-085-0002. However, in LiCoPO_4 with a pH number of 6, there are only a few peaks that similar with JCPDS 00-085-0002. This indicates that the LiCoPO_4 material has been formed, the peak in the

narrow diffraction pattern indicates that the crystal size formed is larger and the pure phase[9–11].



(a)



(b)

Figure 6. FTIR spectra of LiCoPO_4 powder

FTIR analysis was used to determine the groups formed on LiCoPO_4 particles. Figure 6 show FTIR spectra from LiCoPO_4 particles. The vibrational band at 650 cm^{-1} is ascribed to the $\text{V}_4(\text{F}_2)\text{PO}_4^{3-}$ mode of the phosphate (PO_4) group. The broad characteristic peaks at 1017 and 1300 cm^{-1} are attributed to the survival of the $\text{P}=\text{O}$ stretching vibration in PO_4^{3-} and the $\text{P}-\text{O}-\text{P}$ stretching vibration in the HPO_4^{2-} group, respectively. The SEM-EDX characterization have been carried out.

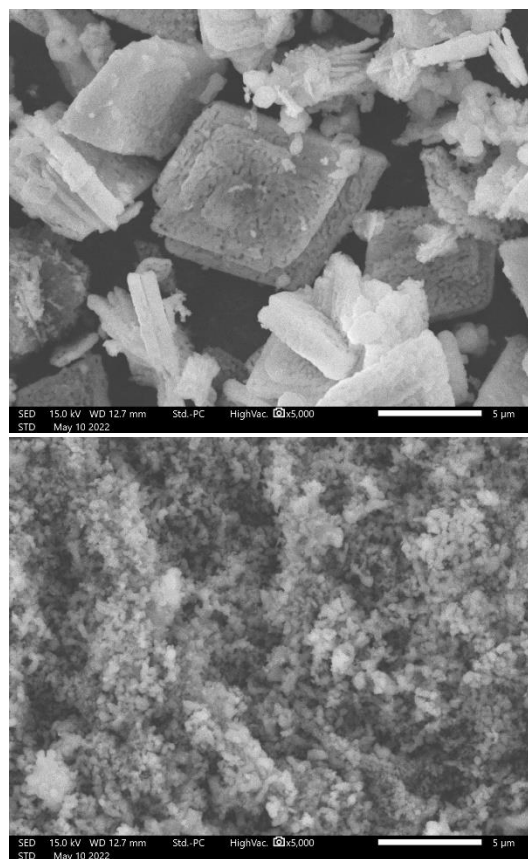


Figure 7. SEM images and EDX results of LiCoPO_4 powder

Figure 7 shows an electron microscope scan (SEM) image of a LiCoPO_4 powder. The morphological shape between the 2 samples is different from LiCoPO_4 with a pH number 4 is in the form of polymorph. Compared to those with a pH number of 6, have a spherical morphological shape. and have different particle size. The particle size of LiCoPO_4A is about 5 microns and LiCoPO_4B is about 0.5 microns[12]. Both have the same purity as evidenced by the results of the EDX characterization in table 2.

Table 2. EDX analysis of LiCoPO_4 samples

LiCoPO ₄ A			LiCoPO ₄ B		
Element	Mass %	Atom %	Element	Mass %	Atom %
O	56.58 ±0.95	79.35 ±1.33	O	45.51 ±1.19	71.30 ±1.86
P	12.00	8.69±	P	14.37	11.63

	± 0.41	0.30		± 0.61	± 0.49
Co	31.42 ± 1.53	11.96 ± 0.58	Co	40.12 ± 2.30	17.07 ± 0.98
Total	100.00	100.00	Total	100.00	100.00

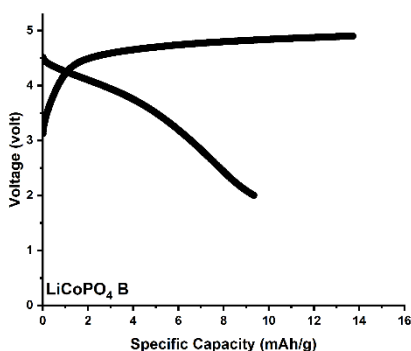
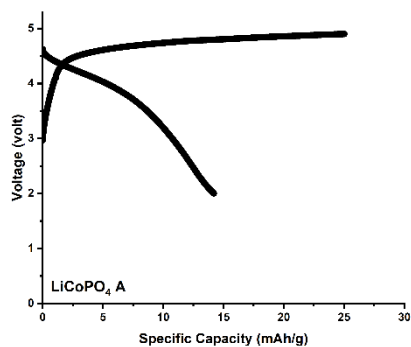


Figure 8. Electrochemical performance results of LiCoPO_4 powder

Figure 8 shows the electrochemical performance of LiCoPO_4 from various variations. Cells were analyzed by measuring the charge-discharge capacity of LiCoPO_4 applied as the cathode. LiCoPO_4 A shows the specific discharge capacity of 14.2 mAh/g and LiCoPO_4 B shows the specific discharge capacity of 9.3 mAh/g with voltage range 2 – 4.95 volt.

5. Conclusion

LiCoPO_4 material was successfully prepared from precipitation method. All LiCoPO_4 samples derived from precursor sintering at 600 °C have good crystalline properties. Furthermore, the SEM analysis

indicates LiCoPO_4 A have unique flaky shape and have same particle size of about 5 microns. Based on the EDX analysis, CoPO_4 B have some impurities than CoPO_4 A caused by excess of NaOH, thus the final product of LiCoPO_4 A and LiCoPO_4 B have different X-ray diffraction pattern. The LiCoPO_4 material have high voltage range in 2 – 4.95 volt. The synthesis of LiCoPO_4 is considered promising to be further developed as cathode material in lithium-ion battery cell.

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Author Contribution: Anjas Prasetya Hutama wrote the manuscript. Yazid Rijal Azinuddin carried out the experiment. Cornelius Satria Yudha who found the idea of the project.

References

- [1] Zaghib, K., Dontigny, M., Guerfi, A., Charest, P., Rodrigues, I., Mauger, A., and Julien, C. M., 2011, Safe and fast-charging Li-ion battery with long shelf life for power applications, *J. Power Sources*, 196 (8), 3949–3954.
- [2] Nitta, N., Wu, F., Lee, J. T., and Yushin, G., 2015, Li-ion battery materials: Present and future, *Mater. Today*, 18 (5), 252–264.
- [3] Mahmoud, B. A., Mirghni, A. A., Oyedotun, K. O., Momodu, D., Fasakin, O., and Manyala, N., 2020, Synthesis of cobalt phosphate-graphene foam material via co-precipitation approach for a positive electrode of an asymmetric supercapacitors device, *J. Alloys Compd.*, 818, 153332.
- [4] Sankar, S. S., Rathishkumar, A., Geetha, K., and Kundu, S., 2020, A Simple Route for the Synthesis of Cobalt Phosphate Nanoparticles for Electrocatalytic Water

Oxidation in Alkaline Medium, *Energy and Fuels*, 34 (10), 12891–12899.

[5] Lapping, J. G., Borkiewicz, O. J., Wiaderek, K. M., Allen, J. L., Jow, T. R., and Cabana, J., 2020, Structural Changes and Reversibility upon Deintercalation of Li from LiCoPO₄ Derivatives, *ACS Appl. Mater. Interfaces*, 12 (18), 20570–20578.

[6] Lee, D. J., Scrosati, B., and Sun, Y. K., 2011, Ni₃(PO₄)₂-coated Li[Ni_{0.8}Co_{0.15}Al_{0.05}]₂ lithium battery electrode with improved cycling performance at 55°C, *J. Power Sources*, 196 (18), 7742–7746.

[7] Ludwig, J., and Nilges, T., 2018, Recent progress and developments in lithium cobalt phosphate chemistry- Syntheses, polymorphism and properties, *J. Power Sources*, 382 (February), 101–115.

[8] Yudha, C. S., Muzayanha, S. U., Hendri, W., Iskandar, F., Sutopo, W., Purwanto, A., Widiyandari, H., Iskandar, F., Sutopo, W., and Purwanto, A., 2019, Synthesis of LiNi_{0.85}Co_{0.14}Al_{0.01}O₂ Cathode Material and its Performance in an NCA / Graphite Full-Battery, *Energies*, 12 (1886), 1886.

[9] Liu, J., Conry, T. E., Song, X., Yang, L., Doeff, M. M., and Richardson, T. J., 2011, Spherical nanoporous LiCoPO₄/C composites as high performance cathode materials for rechargeable lithium-ion batteries, *J. Mater. Chem.*, 21 (27), 9984.

[10] Okita, N., Kisu, K., Iwama, E., Sakai, Y., Lim, Y., Takami, Y., Sougrati, M. T., Brousse, T., Rozier, P., Simon, P., Naoi, W., and Naoi, K., 2018, Stabilizing the Structure of LiCoPO₄ Nanocrystals via Addition of Fe³⁺: Formation of Fe³⁺ Surface Layer, Creation of Diffusion-Enhancing Vacancies, and Enabling High-Voltage Battery Operation, *Chem. Mater.*, 30 (19), 6675–6683.

[11] Zhang, M., Garcia-Araez, N., and Hector, A. L., 2018, Understanding and development of olivine LiCoPO₄ cathode

materials for lithium-ion batteries, *J. Mater. Chem. A*, 6 (30), 14483–14517.

[12] Wu, X., Meledina, M., Tempel, H., Kungl, H., Mayer, J., and Eichel, R. A., 2020, Morphology-controllable synthesis of LiCoPO₄ and its influence on electrochemical performance for high-voltage lithium ion batteries, *J. Power Sources*, 450 (October 2019), 227726.