



Characteristics of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ powders prepared by ultrasonic spray pyrolysis

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ABSTRACT

$\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ powders are prepared by ultrasonic spray pyrolysis from spray solutions with and without sucrose. The precursor powders have a spherical shape and the crystal structure of V_2O_3 irrespective of the concentration of sucrose in the spray solution. The powders post-treated at 700°C have the pure crystal structure of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ phase irrespective of the concentration of sucrose in the spray solution. The $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ powders prepared from the spray solution without sucrose have a non-spherical shape and hard aggregation. However, the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ powders prepared from the spray solution with sucrose have a spherical shape and non-aggregation characteristics. The $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ powders prepared from the spray solution without sucrose have a low initial discharge capacity of 122 mAh g^{-1} . However, the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ powders prepared from the spray solutions with 0.1, 0.3, and 0.5 M sucrose have initial discharge capacities of 141, 130, and 138 mAh g^{-1} , respectively. After 25 cycles, the discharge capacities of the powders formed from the spray solutions with and without 0.1 M sucrose are 70% and 71% of the initial discharge capacities, respectively.

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1. Introduction

$\text{Li}_3\text{V}_2(\text{PO}_4)_3$ is a promising cathode material for lithium secondary batteries. The reversible cycling of all three lithium from $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ would correspond to a theoretical capacity of 197 mAh g^{-1} [1–4]. However, pristine $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ has a low electronic conductivity of about $2.3 \times 10^{-8}\text{ S cm}^{-1}$ at 300 K [1], which presents a major drawback for the practical use of the material.

Carbon coating is an effective way to improve electronic conductivity [3,5–9]. Barker et al. [3] introduced a carbothermal reduction (CTR) method to synthesize $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ using carbon black as the carbon source. In this method, the residual carbon greatly improves the electronic conductivity of the material. Huang et al. [6] reported the nanostructure of a $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite synthesized via a solid-state reaction using resorcinol–formaldehyde as the carbon source. A novel hydrothermal method for the preparation of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ powders was developed by Chang et al [7]. Huang et al. [6], Li et al. [8], and Fu et al. [9] introduced a sol–gel method to synthesize $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ materials.

The electrochemical performance of a cathode in a secondary lithium battery is strongly affected by the powder characteristics such as morphology, specific surface area, crystallinity, and material composition. Spherical powders with narrow size distributions exhibit better electrochemical performance than powders

with irregular morphologies because of their high packing density. Fine-sized cathode powders have been extensively investigated with a view to improve the capacity and power output of secondary lithium batteries. According to previous reports [8,10–12], $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ powders with a small particle size and high surface area are beneficial for capacity improvement.

Spray pyrolysis, which is a gas-phase reaction method, is advantageous for the preparation of cathode powders with a fine size and spherical morphology [13–20]. However, the preparation of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ powders by spray pyrolysis has not been studied. In this study, spherical $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode powders were prepared by spray pyrolysis. The morphological and electrochemical properties of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathode powders prepared by spray pyrolysis under various preparation conditions were investigated.

2. Experimental

$\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode powders were prepared by ultrasonic spray pyrolysis under various preparation conditions. A 1.7-MHz ultrasonic spray generator with six vibrators was used to generate a large amount of droplets. The precursor solution was prepared by dissolving lithium carbonate, vanadium oxide, and ammonium dihydrogen phosphate in the stoichiometric ratio of 3:2:3. The lithium component added to the spray solution exceeded 15% of the stoichiometric amount to facilitate the formation of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ powders. The concentration of sucrose, which was used as the carbon source, was varied from 0 to 0.5 M. The reactor temperature was set at 1300°C . The powders prepared by spray pyrolysis were

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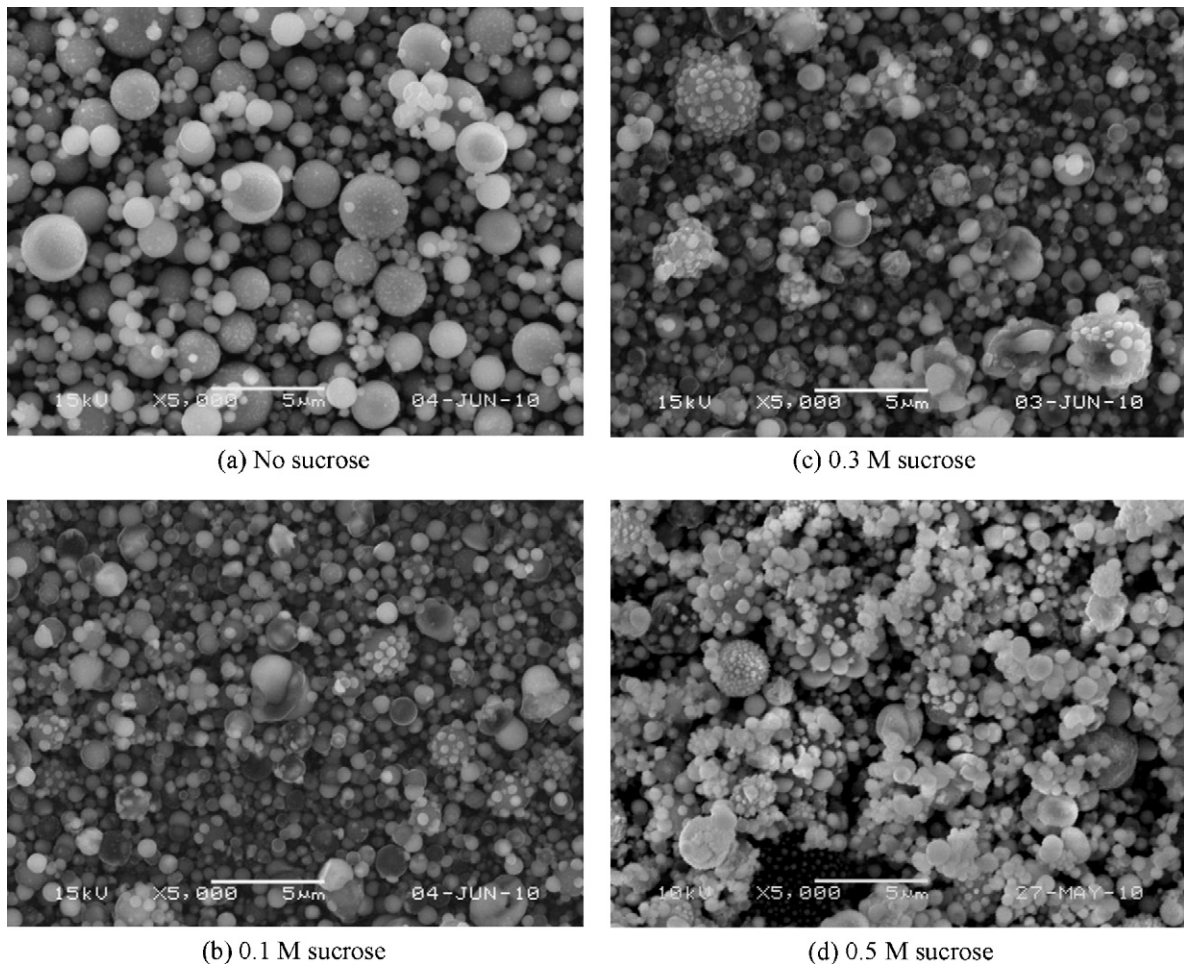


Fig. 1. SEM images of the precursor powders prepared from the spray solutions with and without sucrose.

post-treated at 700 °C for 3 h in an atmosphere of 10% H₂/N₂ reducing gas.

The crystal structures of the precursor and post-treated cathode powders were investigated using X-ray diffractometry (XRD; RIGAKU DMAX-33). The morphological characteristics of the powders were investigated using scanning electron microscopy (SEM; JEOL JSM-6060). The capacities and cycle properties of the Li₃V₂(PO₄)₃/C cathode powders were measured by 2032-type coin. The cathode electrode was prepared from a mixture containing 12 mg of Li₃V₂(PO₄)₃/C compounds and 4 mg of TAB (TAB is a mixture of 3.2 mg of teflonized acetylene black and 0.8 mg of a binder). The loading level of active material is 11 mg cm⁻². Lithium metal and microporous polypropylene film were used as the anode electrode and separator, respectively. The electrolyte was 1 M LiPF₆ in a 1:1 mixture by volume of EC/DEC. The charge/discharge characteristics of the samples were measured through cycling in the 3.0–4.8 V potential range at a constant current density of 0.1 C using a coin cell.

3. Results and discussion

The morphologies of the precursor powders of Li₃V₂(PO₄)₃ and Li₃V₂(PO₄)₃/C obtained by spray pyrolysis are shown in Fig. 1. The precursor powders had a spherical shape irrespective of the concentration of sucrose in the spray solution. However, the inner structure of the precursor powders was affected by the concentration of sucrose. The precursor powders prepared from the spray solution without sucrose had a dense structure.

Fig. 2 shows XRD patterns of the precursor powders prepared by spray pyrolysis. The precursor powders had the same crystal structure as V₂O₃ irrespective of the concentration of sucrose in the spray solution. The Li₃V₂(PO₄)₃ crystal phase was not formed because of the short residence time of the powders in the hot-wall reactor (0.54 s). Therefore, the precursor powders obtained

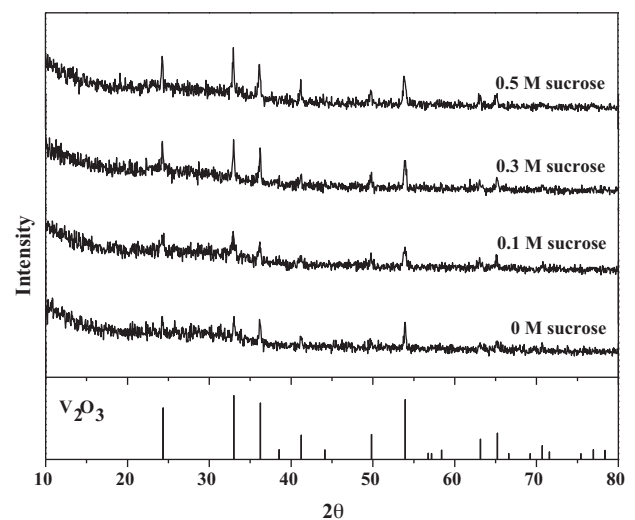


Fig. 2. XRD patterns of the precursor powders prepared from the spray solutions with and without sucrose.

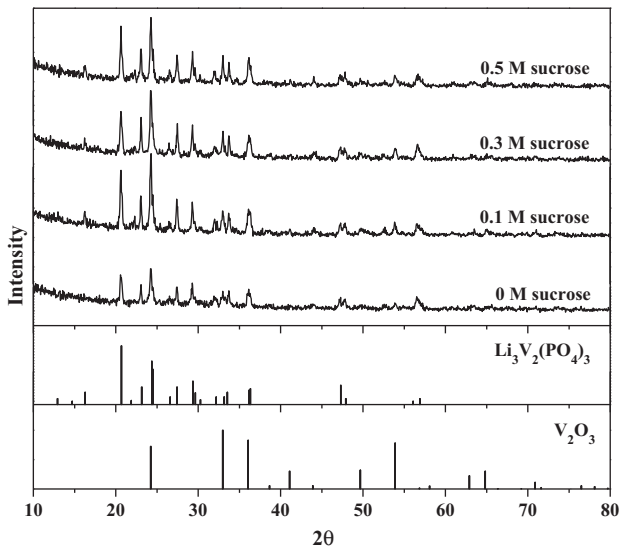


Fig. 3. XRD patterns of the post-treated powders prepared from the spray solutions with and without sucrose.

by spray pyrolysis were post-treated at 700 °C. Figs. 3 and 4 show the crystal structures and morphologies of the post-treated powders. These powders had the pure crystal structure of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ phase irrespective of the concentration of sucrose in the spray solution. However, the mean crystallite size of the pow-

ders as calculated by Scherrer's equation from the half-width of the XRD peak was influenced by the concentration of sucrose in the spray solution. The mean crystallite size of the powders prepared from the spray solution without sucrose was 28 nm. On the other hand, the mean crystallite sizes of the powders prepared from the spray solutions with 0.1, 0.3, and 0.5 M sucrose were 29, 29, and 44 nm, respectively. The morphologies of the powders were also affected by the concentration of sucrose in the spray solution. The powders prepared from the spray solution without sucrose had a non-spherical shape and hard aggregation after post-treatment. However, the spherical shape of the precursor powders prepared from the spray solutions with sucrose was retained after post-treatment. The carbon covering of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ powders prohibited their aggregation during the post-treatment process. Figs. 5 and 6 show transmission electron microscopy (TEM) images of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ powders prepared from the spray solutions with 0.1 and 0.5 M sucrose. The post-treatment temperature was 700 °C. The $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ powders prepared from the spray solution with 0.1 M had irregular crystals coated with carbon. On the other hand, $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ powders with regular shape and submicron size were dispersed in the carbon matrix in the powders prepared from the spray solution with 0.5 M. The carbon matrix prohibited the growth of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ crystals. Fig. 7 shows the results of dot mapping of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ powders as shown in Fig. 6. V, P, and C components are well dispersed inside the powders.

Fig. 8 shows the TG curves of the precursor and $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ powders prepared from the spray solution with 0.5 M sucrose. The

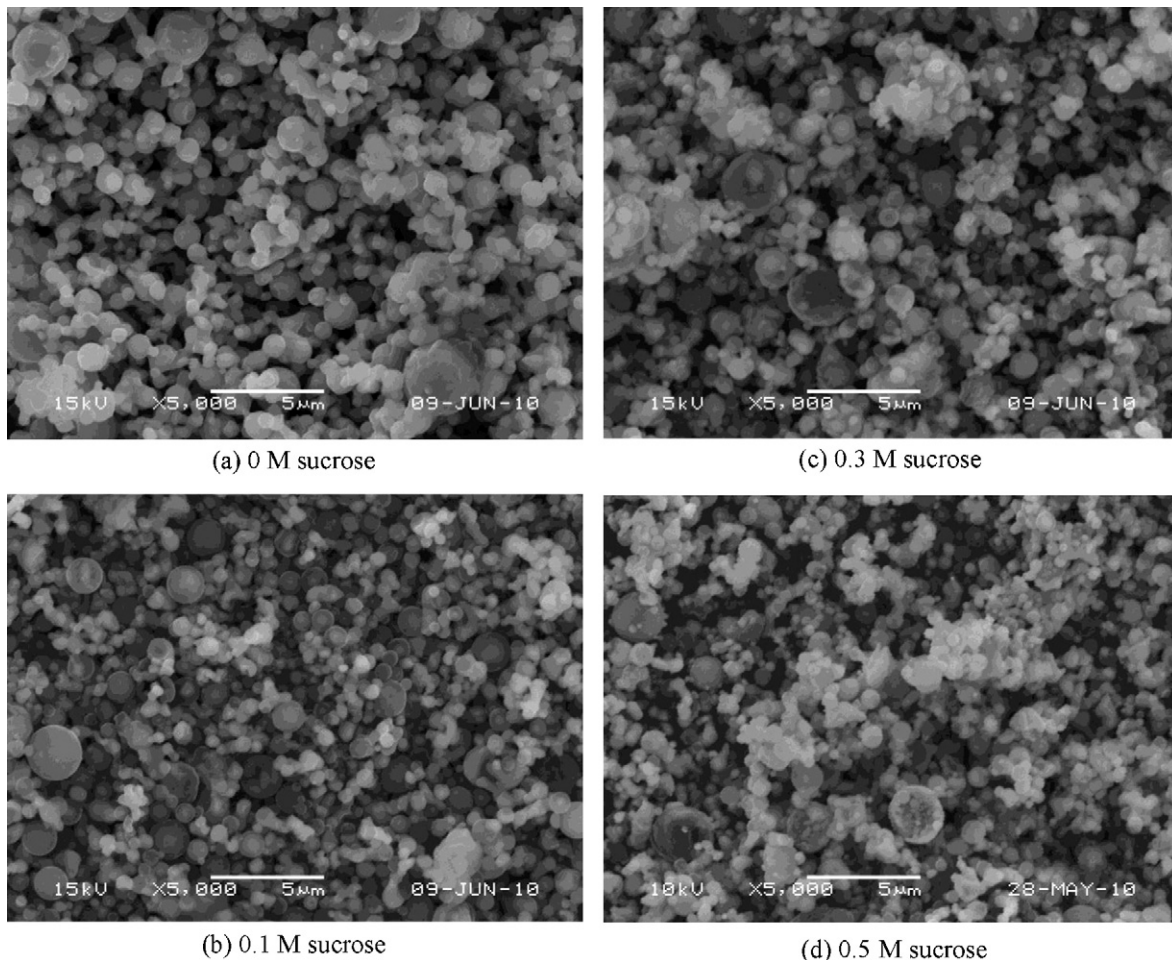


Fig. 4. SEM images of the post-treated powders prepared from the spray solutions with and without sucrose.

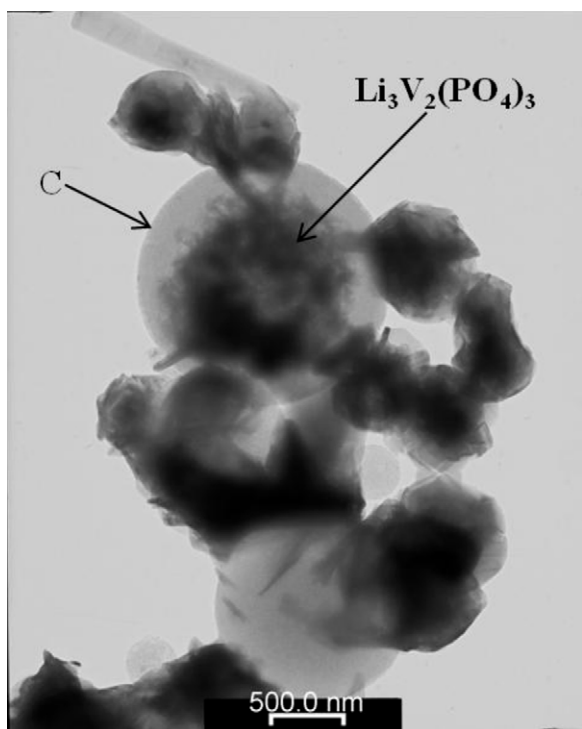


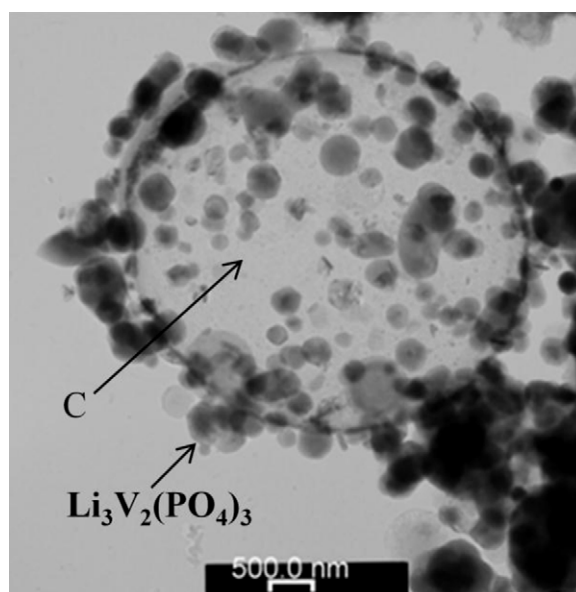
Fig. 5. TEM image of the post-treated powders prepared from the spray solution with 0.1 M sucrose.

TG curves of the precursor powders indicate two weight losses at temperatures below 1000 °C. The first prominent weight loss region from 40 to 250 °C resulted from the loss of adsorbed water. The high weight loss from 350 to 500 °C in the TG curves of the precursor powders can be attributed to the decomposition of the carbon material. However, the weight loss region from 40 to 250 °C, which resulted from the loss of adsorbed water, is not observed in the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ powders. The weight losses of the precursor and the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ powders due to the decomposition of the carbon material were 6.8% and 7.5%, respectively.

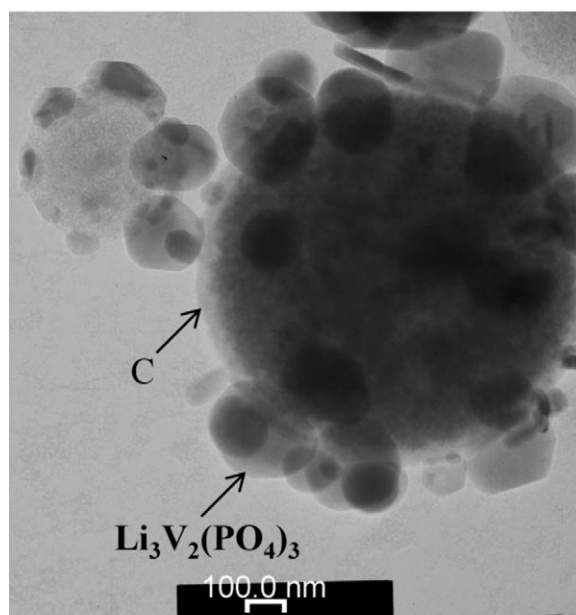
The formation mechanism of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ particle was estimated from the morphologies and crystal structures of the precursor and post-treated powders. One composite particle of the V, P, O, and C components was formed from one droplet by the drying and decomposition process. The composite particle contained fine crystals of V_2O_3 . These crystals reacted with the Li and P components to form the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ phase. The carbon material formed from the decomposition of sucrose in a reducing atmosphere remained in the powder, and thus, $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ powder was obtained.

Fig. 9 shows the initial charge/discharge curves of the precursor and post-treated powders prepared from the spray solutions with and without sucrose. At a constant current density of 0.1 C, the precursor powders obtained from the spray solutions with and without sucrose had low discharge capacities, below 10 mAh g^{-1} . The $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ powders prepared from the spray solution without sucrose had a low initial discharge capacity of 122 mAh g^{-1} . However, the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ powders prepared from the spray solutions with 0.1, 0.3, and 0.5 M sucrose had initial discharge capacities of 141, 130, and 138 mAh g^{-1} .

Fig. 10 shows the cycle properties of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ powders at a constant current density of 0.1 C. The discharge capacities of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ powders prepared from the spray solution without sucrose decreased from 122 to 86 mAh g^{-1} by the 25th cycle. However, the discharge capacities of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ powders prepared from the spray solution



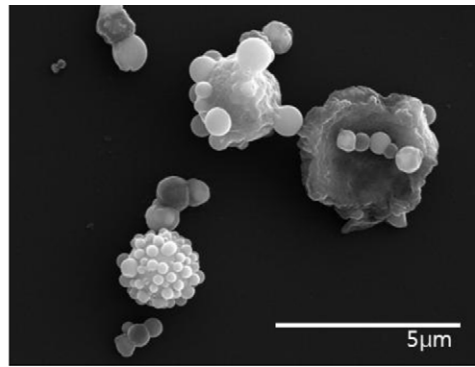
(a) low resolution



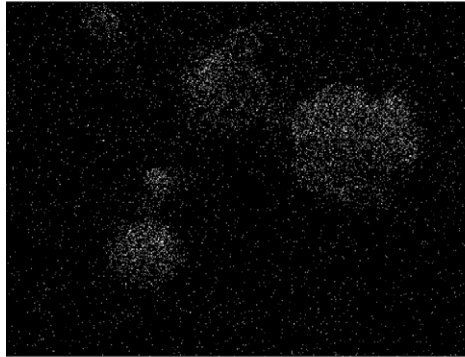
(b) high resolution

Fig. 6. TEM images of the precursor and post-treated powders prepared from the spray solution with 0.5 M sucrose.

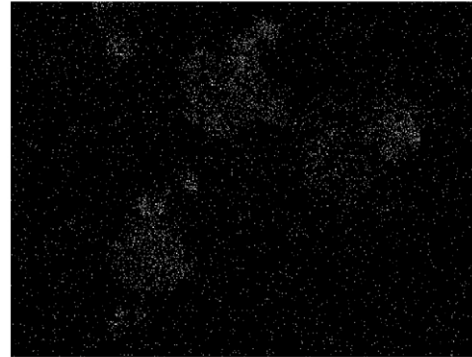
with 0.1 M sucrose decreased from 141 to 100 mAh g^{-1} by the 25th cycle. After 25 cycles, the discharge capacities of the powders prepared from the spray solutions with and without 0.1 M sucrose were 70% and 71% of the initial discharge capacities, respectively. The $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ powders prepared by spray pyrolysis have poor cycle properties. However, the electrochemical properties of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode powders prepared by spray pyrolysis could be optimized by changing the preparation conditions, such as excess amount of Li component, precursors of Li, V, P, and C components, preparation temperature, flow rate of the carrier gas, type of the carrier gas and post-treatment temperature. In this study, the possibility of the preparation of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode powders in the spray pyrolysis is studied.



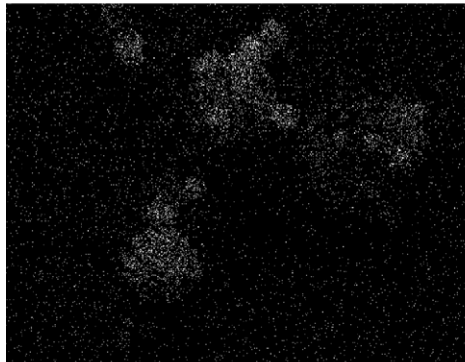
(a) SEM



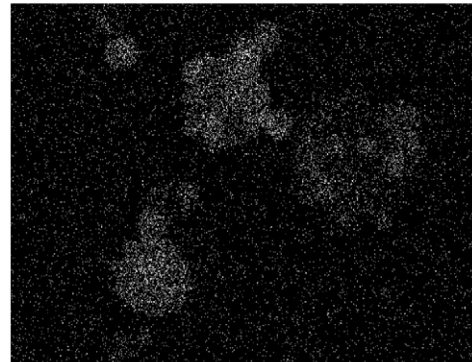
(b) V



(c) C



(d) O



(e) P

Fig. 7. Dot mappings of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ powders prepared by spray pyrolysis.

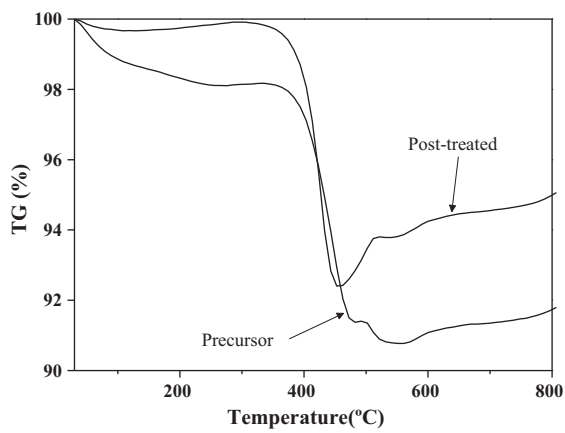


Fig. 8. TG curves of the precursor and post-treated $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ powders.

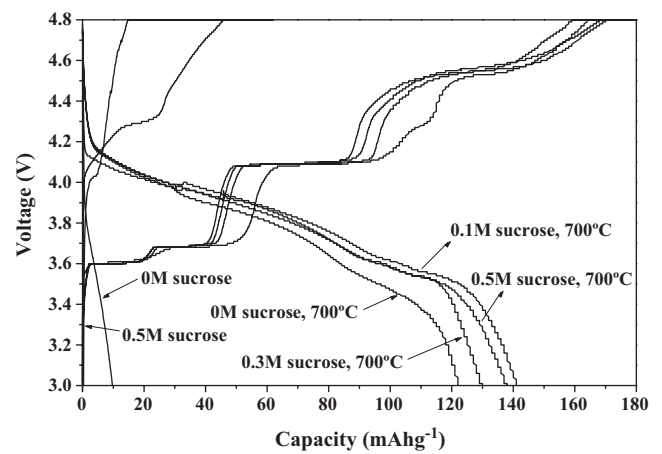


Fig. 9. Initial charge/discharge curves of the precursor and post-treated powders prepared from the spray solutions with and without sucrose.

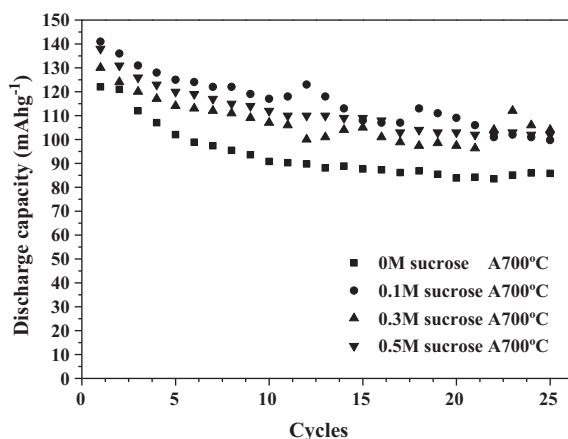


Fig. 10. Cycle properties of the post-treated powders prepared from the spray solutions with and without sucrose.

4. Conclusions

Spherical $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ powders were prepared by spray pyrolysis from a spray solution containing sucrose. Sucrose was used as the carbon source. The precursor powders prepared by spray pyrolysis were transformed into single-crystal-phase $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ powders at the low post-treatment temperature of 700°C . The carbon source improved the morphological characteristics of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ powders. The $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ powders prepared from the spray solution with 0.1 M had irregular crystals coated with carbon. On the other hand, $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ powders with regular shape and submicron size were dispersed in the carbon matrix in the powders prepared from the spray solution with 0.5 M. The carbon matrix prohibited the growth of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ powders.

$\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ powders had higher initial discharge capacities compared to $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ powders.

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