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Electrochemistry of LiV$_3$O$_8$ Nanoparticles Made by Flame Spray Pyrolysis

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LiV$_3$O$_8$ nanoparticles (primary particles with ca. 50 nm diameter) have been synthesized by flame spray pyrolysis (FSP). The powder was characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and galvanostatic cycling. The initial discharge capacity of the LiV$_3$O$_8$ nanoparticles is 271 mAh g$^{-1}$ when discharged from its open-circuit potential to 2.0 V vs Li/Li$^+$ at a specific current of 100 mA g$^{-1}$ under ambient conditions. The nanoparticles retained a specific discharge capacity of 180 mAh g$^{-1}$ beyond 50 cycles. This paper describes the synthesis route as well as the characterizations of the FSP-produced LiV$_3$O$_8$ nanoparticles.

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Lithium-ion (Li-ion) rechargeable batteries are currently used in commercially available electronic devices due to their high cell voltage and energy density. LiCoO$_2$ is the current cathode material of choice; however, there is a demand for alternative cathode materials due to the high cost,$^{1,2}$ relative toxicity, and safety concerns of this material. LiV$_3$O$_8$ as a cathode material has the advantages of higher specific charge, lower cost, and better safety features.$^{3}$ An extensive amount of study has been conducted in topics including the material's degree of crystallinity,$^{4,5}$ the origin of capacity fading,$^{6}$ numerous synthesis methods,$^{7,8,9}$ and the polymer binder content in the composite electrode.$^{10,11}$

The power density of Li-ion batteries can be improved by increasing the interfacial area between the electrolyte and the active material. The use of oxide nanoparticles as cathode materials in Li-ion batteries presents numerous opportunities and challenges.$^{12}$ There is an opportunity to increase the power density and at the same time the challenge in dealing with increased electrode-electrolyte side reactions. Both phenomena are due to the higher specific surface area of the nanoparticles compared to their µm-sized counterparts.

Flame spray pyrolysis (FSP) is a process which can produce oxide nanoparticles at an industrial scale. It is a flexible and scalable process$^{13,14}$ which is already used to produce fine powders for use as catalysts, coatings, and dental fillers, to name a few. FSP has been used previously to produce electrochemically active crystalline oxide nanoparticles with a spinel structure (LiMn$_2$O$_4$, LiFe$_2$O$_4$, and Li$_4$Ti$_5$O$_12$)$^{15}$ It is demonstrated that FSP is a potentially cost-effective process to produce electrochemically active nanosized spinel materials of controlled composition, crystallinity, and morphology. Furthermore, FSP has also been used to produce LiCoO$_2$. All these advantages make FSP an attractive process to produce nanosized cathode materials.

This paper describes the synthesis of nanosized LiV$_3$O$_8$ material by FSP and presents the electrochemical characterization of this powder.

**Experimental**

The experimental setup for FSP is described elsewhere.$^{14}$ The precursor used for the flame synthesis was prepared by first dissolving 9.17 g of vanadium (V) oxyptripropoxide (Aldrich, 98%) into 18.7 mL of diethylene glycol (Fluka). This solution was then stirred into 19.0 mL of toluene (Riedel-de Haén) and 12.5 mL of 1 M lithium tert-butoxide solution in tetrahydrofuran (Aldrich). Therefore, the precursor solution contains a molar ratio of Li to V of 1 to 3. Subsequently, this precursor was injected at a rate of 3 mL min$^{-1}$ through the reactor nozzle and dispersed with 5 L min$^{-1}$ of oxygen into a fine spray. A pressure of 1.5 bar was maintained across the nozzle tip. A premixed flame composed of 1 L min$^{-1}$ of methane and 2 L min$^{-1}$ of oxygen was maintained to ignite and support the combustion of the spray. A sheath gas of 5 L min$^{-1}$ of oxygen surrounding the flame was used to ensure complete combustion. The dry powder was collected by placing a glass fiber filter (GF/D, 26 µm thick) above. Gas and nitrogen at a scan rate of 5 L min$^{-1}$ was done with a vacuum pump. The reactor was cooled. The Topas 2 software. The XRD measurement was performed at a temperature of 110°C overnight in order to remove the
solvent and form a composite electrode. The active material, LiV$_2$O$_5$, accounted for 70 wt % of the electrode composite.

Electrodes with a diameter of 13 mm were punched out and dried in a vacuum chamber at 120°C overnight. They were then assembled in test cells similar to coin cells, where they functioned as the working electrode. Lithium metal (Aldrich, 99.9%) was used as both the counter and reference electrodes. It was separated from the working electrode by a 1 mm thick fiberglass separator soaked in 500 μL of electrolyte [ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 by mass), with 1 M LiPF$_6$ (Merck LP30, Selectipur)]. Cells were assembled in an argon-filled glove box with less than 1 ppm of oxygen and water contents.

Both the cyclic voltammetry (CV) and galvanostatic measurements were performed by means of a computer-controlled cell capture (CCGC) system (Astrol Electronics AG, Oberrohrdorf, Switzerland), by discharging (insertion of lithium-ions) first from respective open-circuit potential. CV measurements were conducted in the range of 1.5–4.0 V vs Li/Li$^+$ at a potential scan rate of 0.1 mV s$^{-1}$. Unless otherwise noted, the electrodes were cycled galvanostatically in the range of 2.0–4.0 V vs Li/Li$^+$ at a specific current of 100 mA g$^{-1}$ (based on the oxide weight). In order to promote complete discharge-charge at the respective potential limits, a potential static step was included until the current was 10% of the current used in the galvanostatic step.

Results and Discussion

Material characterization.—An initial investigation into the synthesis capabilities of FSP was conducted by varying the molar concentration of the precursor solutions. Six different powders were produced from precursors with molar concentrations ranging from 1.50 to 0.25 M, with variations of 0.25 M between each precursor solution. Little change in SSA was seen for powders flame-sprayed from precursor solutions with 1.50 to 0.50 M concentrations, as the BET SSA varied from 33.6 to 39.5 m$^2$ g$^{-1}$. A significant increase in the SSA was only seen for powders flame-sprayed from the precursor solution with 0.25 M concentration. Here, a BET SSA of 67.4 m$^2$ g$^{-1}$ was measured, suggesting that even smaller particles are possible when more dilute precursor solutions are used. From an industrial viewpoint, a higher concentration is more attractive due to the increase in powder production rate.

Material and electrochemical characterizations of the powders produced by FSP of the 1.00 M precursor solution are presented in this work as they are representative of the properties of the FSP-produced LiV$_2$O$_5$ nanoparticles. Temperatures before the filter were measured between 150 and 200 °C and amorphous powder with some crystalline features (see Fig. 1a) was collected. By moving the filter paper closer to the flame, the temperatures increased to a range between 250 and 300 °C, and so the powder was annealed above the flame on the filter (see Fig. 1b). The total production time of this batch lasted about 30 min; therefore, the annealing of this material was no longer than 30 min. The crystallinity of this powder can be further refined by subsequent annealing in an oven for 30 min at 350°C (see Fig. 1c). The BET SSA of the amorphous powder was measured to be 35.9 m$^2$ g$^{-1}$. This area decreased with increasing heat treatment: 30.5 and 27.5 m$^2$ g$^{-1}$ for the powder annealed on the filter and subsequently in the oven, respectively.

XRD patterns of the LiV$_2$O$_5$ nanoparticles are shown in Fig. 1. For the as-synthesized material (Fig. 1b) a monoclinic phase is present, while an amount of impurity is also detectable. For the monoclinic phase, the diffraction peak positions for the LiV$_2$O$_5$ nanoparticles (lattice constants $a = 6.634$ Å, $b = 3.593$ Å, $c = 11.998$ Å, and $\beta = 107.830^\circ$) match well with those of the known monoclinic layered-type LiV$_2$O$_5$ (lattice constants $a = 6.68$ Å, $b = 3.60$ Å, $c = 12.03$ Å, and $\beta = 107.83^\circ$; JCPDS Card No. 72-1193). The corresponding hkl indices are given in Fig. 1. Analysis of the XRD data in Fig. 1b indicates that the powder is crystalline; however, LiV$_2$O$_5$ is detectable in Fig. 1b as an impurity in the powder, as seen by the peak between 12 and 13° and also in related work. The intensity of this peak significantly decreases upon subsequent heat treatment (Fig. 1c). When the Debye–Scherer equation was applied to the (100), (020), and (003) peaks in Fig. 1b, the crystallite size of the LiV$_2$O$_5$ nanoparticles was calculated as 23.9, 24.0, and 27.5 nm, respectively. The average crystal size is therefore about 25 nm.

The overall morphology of the LiV$_2$O$_5$ nanoparticles of the crystalline powder annealed on the filter was investigated by SEM and TEM. The average primary particle diameter observed in the SEM image (Fig. 2a) is approximately 50 nm. Moreover, the particles are agglomerated in chain-like aggregates of primary particles connected by sintered necks and secondary particles clumped together, obviously by van der Waals surface forces. High-resolution transmission electron microscope (HRTEM) images of the LiV$_2$O$_5$ nanoparticles synthesized via FSP are shown in Fig. 2b. The strongly crystalline structure of the flame-spray pyrolyzed LiV$_2$O$_5$ nanoparticles is well-defined by the highlighted lattice constant c (1.2 nm). Moreover, the corresponding selected area electron diffraction (SAED) pattern for the flame-spray pyrolyzed LiV$_2$O$_5$ nanoparticles is shown in the inset of Fig. 2b, revealing the hkl indices of the LiV$_2$O$_5$ nanoparticles, which is in accordance with the monoclinic phase of LiV$_2$O$_5$ (JCPDS Card No. 72-1193). A Li/V ratio in the powder was calculated to be 1.01/3.00 based on ICP-OES measurements. When considering the accuracy of the analytical method, this is in good agreement with the 1/3 stoichiometric ratio of Li/V used in the solution precursor prepared prior to the flame synthesis. Because of the excellent agreement between the XRD data and the known monoclinic layered-type LiV$_2$O$_5$, the analysis by HRTEM, and a calculated Li/V ratio of 1.01/3.00, this powder consists primarily of LiV$_2$O$_5$ and the material and electrochemical contributions of other phases are assumed to be insignificant. Impurities such as Li$_3$V$_2$O$_5$ could, however, have a minor influence on the electroactivity of the powder.

The BET SSA of the as-synthesized crystalline powder was measured to be 30.5 m$^2$ g$^{-1}$. This is much higher than those values (<5 m$^2$ g$^{-1}$) for subμm particles that are produced by spray drying, and shows that FSP is superior when small particles are required at an industrial scale. In order to confirm the degree of porosity in the as-synthesized LiV$_2$O$_5$ material, a standard N$_2$
adsorption–desorption isotherm test was carried out on a Micromeritics Tristar 3000 adsorption apparatus at 77 K. Figure 3 shows the pore size distribution curve calculated from the adsorption points using the Barrett–Joyner–Halenda (BJH) algorithm. Only the presence of macropores is evidenced here, resulting from the particle interfaces. The average pore diameter calculated from the BJH adsorption curve was 15.3 nm, which is about one third of the size of a LiV₃O₈ particle. The low degree of porosity was further verified by the corresponding N₂ adsorption–desorption isotherms (see the inset of Fig. 3), where no hysteresis loop was observed at low relative pressures, indicating the presence of macropores only.

Electrochemical characterization.—The electrochemistry of the LiV₃O₈ crystalline nanoparticles is studied only for the powder annealed during flame synthesis. Cyclic voltammograms of the LiV₃O₈ powder are shown in Fig. 4 for the second and 20th cycle. The oxidative and reductive peaks are seen to diminish rapidly from the second to the 20th cycle due to capacity fading. The shapes of these two voltammograms are roughly the same. Assuming there is no second phase developing and simultaneously not modifying the cyclic voltammogram, than no significant change in the crystallography is expected between these cycles. This would indicate that the decrease in the specific capacity is likely due to the loss of the electrochemically active mass. Possible losses could be due to the dissolution of LiV₃O₈ into the electrolyte, formation of an insulating passivation layer between the active material particles and the electrolyte, or the degradation of the electrode composite resulting in a contact loss, possibly due to the growth of the insulating passivation layer. A simple qualitative observation of the dissolution of the powder was done by placing the powder into a 1 M LiPF₆, EC:DMC (1:1 by weight) electrolyte. After 1 month of storage in the liquid electrolyte, the initially clear solution was seen to be colored. This confirms that a dissolution of the powder occurs, but not necessarily at a rate that would significantly influence capacity fading. Tanguy et al. associate the capacity fading with the buildup of a passivation layer between the electrode and electrolyte, which was seen to contain organic species as indicated by X-ray photoelectron spectroscopy measurements. This is likely occurring during the cycling of the electrodes presented in this work, as the active material is similar to the material used by Tanguy et al. in terms of average particle size.

Upon repeated cycling, a broad peak at around 3.1 V in the 20th cycle appears. This indicates that an additional oxidative reaction is occurring at a higher potential value than initially experienced. A similar event was experienced by another group, but its occurrence also was not understood.

![Figure 3](image-url) (Color online) Pore size distribution curve of the FSP-made LiV₃O₈ nanoparticles, calculated from the adsorption points using the BJH algorithm. Inset shows the corresponding N₂ adsorption–desorption isotherms.

![Figure 4](image-url) (Color online) Cyclic voltammograms of LiV₃O₈ at the second and 20th cycle at 0.1 mV s⁻¹.
A cycling procedure was followed for potential cutoffs of 1.5, 2.0, and 4.0 V. The high BET SSA of the material presented in this work (30 m² g⁻¹) likely leads to a substantial decrease in the specific capacity above 100 mA h g⁻¹. This is likely occurring because the increase in lithium extraction has an irreversible reaction mechanism against lithium insertion. This is particularly apparent during high current densities where capacity fading is seen to increase in comparison to the other two measurements. This decline leads to a lower capacity within 50 cycles, where the specific current returns to its original value of 100 mA g⁻¹. Capacity fading is clearly strongest for specific current densities greater than 1000 mA g⁻¹ for potential cutoffs of 1.5 and 4.0 V.

The influence of the particle size is a likely candidate for the pronounced capacity fading seen in our case. The work of Kannan and Manthiram presents LiV₃O₈ particles with sizes of ~4 μm produced via a solution dispersion method. This powder was measured to have a specific capacity of 230 mA h g⁻¹ with no significant fading after 20 cycles when cycled at 0.5 mA cm⁻² between 2.0 and 3.5 V. The improved cycling of this material over the one presented in our paper is likely better because the μm-sized particles experience weaker capacity-decreasing side reactions than the nanosized particles do. To overcome this disadvantage, Chew et al. coated their LiV₃O₈ nanoparticles (50 nm from XRD) produced via a low-temperature solution route with polypyrrole (PPy). The result is almost no capacity fading upon cycling; a reversible capacity of 183 mA h g⁻¹ after 100 cycles with PPy-coated material as compared to a decrease from over 200 to 110 mA h g⁻¹ for uncoated material. Both materials were cycled at 40 mA g⁻¹ between 1.50 and 3.85 V. This result suggests that coating with a conductive binder can significantly inhibit the capacity fading for LiV₃O₈ nanoparticles and would likely decrease the rate of formation of a passivation layer expected at the electrode/electrolyte interface.

In this work, the charge efficiency (%) shown in Fig. 5 is defined as follows

\[
\text{Charge efficiency (\%) } = \left( 100 - \frac{C_{\text{c}} - C_{\text{d}}}{C_{\text{c}}} \times 100 \right) \quad [1]
\]

where \(C_{\text{c}}\) and \(C_{\text{d}}\) are the charge and discharge capacities (specific capacity), respectively.

Figure 6 summarizes the second, tenth, and 50th electrochemical lithiation (discharge)/delithiation (charge) capacity data for the LiV₃O₈ electrode. The calculated specific capacities were solely based on the active material, LiV₃O₈ nanoparticles. The LiV₃O₈ electrode shows a capacity fading behavior upon prolonged cycling. However, the LiV₃O₈ electrode still maintained fairly high Li-ion
insertion/deinsertion capacity even after 50 cycles, retaining a discharge capacity of 180 mAh g\(^{-1}\). The shapes of the discharge-charge plots were similar even after 50 cycles. Therefore, the potentials at which the Li-ion insertion/deinsertion occurs are roughly the same and the likely reason for capacity loss is not due to major changes in the oxide’s crystal structure.

**Conclusion**

Li\(^2\)V\(_3\)O\(_8\) nanoparticles with an average primary particle size of approximately 50 nm have been synthesized by FSP. This is an attractive process as it can be scaled to industrial production levels. An initial variation of the lab-scale production capability is presented. Material and electrochemical characterizations were conducted for the Li\(^2\)V\(_3\)O\(_8\) nanoparticles. The Li\(^2\)V\(_3\)O\(_8\) nanoparticles produced in the dry phase by FSP have a relatively high maximum charge capacity (>300 mAh g\(^{-1}\)); however, it is seen to have a stronger capacity fading (>2% per cycle beyond 50 cycles) when compared to μm-sized particles\(^{52}\) and nanoparticles treated with conductive binders.\(^{52}\) Possible sources of the capacity fading of the electrodes containing the FSP-produced nanoparticles are the formation of a passivation layer at the electrode/electrolyte interface, dissolution of the active material into the electrolyte, and/or insufficient engineering to optimize the electrode composition. Nevertheless, Li\(^2\)V\(_3\)O\(_8\) nanoparticles are promising as cathode materials for use in lithium batteries, and further investigations will follow.

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