

Short communication

## Low temperature synthesis and electrochemical behavior of $\text{LiV}_3\text{O}_8$ cathode

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### Abstract

$\text{LiV}_3\text{O}_8$  cathode has been synthesized by two simple low temperature methods without involving the melting of  $\text{V}_2\text{O}_5$  and characterized by X-ray diffraction, scanning electron microscopy (SEM), discharge–charge measurements in lithium cells and differential scanning calorimetry (DSC). While the first method involves the heating of the components in  $\text{H}_2$  at  $500^\circ\text{C}$  followed by in  $\text{N}_2$  at  $600^\circ\text{C}$ , the second method involves the dispersion of the components in methanol followed by evaporating the solvent and heating at  $500^\circ\text{C}$  in  $\text{N}_2$  atmosphere. The samples exhibit a high capacity of around  $230\text{ mAh g}^{-1}$  at  $0.5\text{ mA cm}^{-2}$  and  $25^\circ\text{C}$  in a narrow voltage range of 2–3.5 V with excellent cyclability at  $-30$  to  $60^\circ\text{C}$ . Additionally, the samples exhibit superior safety characteristics compared to the currently used  $\text{LiCoO}_2$  cathode as indicated by the absence of exothermic peaks (DSC) up to  $450^\circ\text{C}$  in the charged state.

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### 1. Introduction

Lithium ion batteries have become attractive for portable electronic devices due to their higher cell voltage and energy density compared to the other rechargeable systems. Lithium ion cells presently use the layered  $\text{LiCoO}_2$  cathode, but only 50% of its theoretical capacity could be utilized in practical cells due to chemical and structural instabilities at deep charge with  $(1-x) < 0.5$  in  $\text{Li}_{1-x}\text{CoO}_2$  [1]. Moreover, Co is expensive and relatively toxic, and charged  $\text{Li}_{1-x}\text{CoO}_2$  poses safety concerns due to the highly oxidized nature of the  $\text{Co}^{3+/4+}$  couple and an overlap of the  $\text{Co}^{3+/4+} : 3d$  band with the top of the  $\text{O}^{2-} : 2p$  band. These difficulties have generated enormous interest in the development of alternative cathode materials. In this regard, layered oxide solid solutions, such as  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ ,  $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$  and  $\text{Li}(\text{Li}, \text{Ni}, \text{Mn}, \text{Co})\text{O}_2$  have become appealing as they lower the cost and offer improved safety characteristics [2–5]. Additionally, cation-substituted

spinel manganese oxides [6] and conductive carbon incorporated olivine iron phosphate [7,8] are being intensively pursued.

Vanadium oxides are attractive alternatives as vanadium is known to exist in a wide range of oxidation states from +2 as in VO to +5 as in  $\text{V}_2\text{O}_5$  and the vanadium oxides have the potential to offer much higher capacities. Among the various known vanadium oxides,  $\text{VO}_2(\text{B})$ ,  $\text{V}_6\text{O}_{13}$ ,  $\text{V}_2\text{O}_{5-\delta}$ ,  $\text{V}_2\text{O}_5$  and  $\text{LiV}_3\text{O}_8$  have been found to show interesting cathode properties [9–22] although they could not be combined with the presently used carbon anodes in lithium ion cells as they do not contain extractable lithium. Among these oxides,  $\text{LiV}_3\text{O}_8$  has a layered structure and has been investigated as a cathode material for nearly 20 years, after the first investigation by Panero et al. [18]. The synthesis generally involves a melting of one of the components ( $\text{V}_2\text{O}_5$ ) by heating to  $680^\circ\text{C}$  [18]. In general, the synthesis method has been found to strongly influence the electrochemical performance of  $\text{LiV}_3\text{O}_8$ .

Liu et al. [17] have reported the synthesis of  $\text{LiV}_3\text{O}_8$  by heating at various temperatures ( $370$ ,  $450$  and  $550^\circ\text{C}$ ) a precursor obtained with  $\text{LiOH}$  and  $\text{V}_2\text{O}_5$  in  $\text{NH}_4\text{OH}$ , but the material has been found to exhibit severe capacity fade. For example, the capacity value of the  $370^\circ\text{C}$  heated sample decreases from  $274$  to  $257\text{ mAh g}^{-1}$  within 15 discharge–charge cycles in the

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voltage range of 1.8–4 V at a current density of  $0.3 \text{ mA cm}^{-2}$ . The 450 and 550 °C samples with a lower initial capacity values also exhibit similar capacity fade within 15 cycles (264 to 245 and 192 to 175  $\text{mAh g}^{-1}$  for the 450 and 550 °C samples, respectively). More recently, Xu et al. [19] have reported fairly good cyclability, but the synthesis involves a complicated hydrothermal route, followed by heat-treatment at different temperatures in the range of 300–600 °C. In another recent report [22],  $\text{LiV}_3\text{O}_8$  prepared by a mechanochemical route followed by heat-treatment at 200–400 °C has been found to exhibit a high capacity of  $>300 \text{ mAh g}^{-1}$ , but with a continuously sloping discharge voltage profile.

We present here the synthesis of  $\text{LiV}_3\text{O}_8$  by two simple low temperature (500 or 600 °C) methods without involving the typical melting of  $\text{V}_2\text{O}_5$ , their characterization and electrochemical behavior in lithium cells. The samples exhibit excellent cyclability in a wide temperature range with a reversible capacity of around  $230 \text{ mAh g}^{-1}$  and a nearly flat voltage profile in a narrow voltage range of 2–3.5 V at a high current density of  $0.5 \text{ mA cm}^{-2}$ .

## 2. Experimental

$\text{LiV}_3\text{O}_8$  was synthesized by two different methods. In the first method, a stoichiometric mixture of  $\text{LiOH}\cdot\text{H}_2\text{O}$  and  $\text{V}_2\text{O}_5$  was heated in hydrogen atmosphere at 500 °C for 12 h followed by in nitrogen atmosphere at 600 °C for another 12 h. This method is hereafter referred to as solid state method. In the second method, stoichiometric quantities of ammonium metavanadate and lithium hydroxide were dispersed in methanol by stirring for 3 h, the solvent was evaporated on a hot plate, and the homogenized dry mass was then heated at 500 °C in nitrogen atmosphere for 6 h. This method is hereafter referred to as solution dispersion method.

Thermogravimetric analysis (TGA) of the precursors and the synthesized  $\text{LiV}_3\text{O}_8$  was carried out with a Perkin-Elmer Series 7 thermal system in nitrogen atmosphere with a heating rate of  $2^\circ\text{C min}^{-1}$ . The synthesized samples were characterized by X-ray diffraction. The cathodes for lithium cells were fabricated by mixing the  $\text{LiV}_3\text{O}_8$  powder, Denka black carbon, and polytetrafluoroethylene (PTFE) binder in a weight ratio of 75:20:5. The electrochemical cells (CR2032 coin cells) were assembled with the cathodes thus fabricated, metallic lithium anode, polyethylene separator and 1 M  $\text{LiPF}_6$  in 1:1 ethylene carbonate (EC) and diethyl carbonate (DEC) electrolyte. Cells for low temperature study were fabricated with  $\text{LiPF}_6$  in 3:5:4:1 EC, DEC, dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC) electrolyte. The electrochemical performances were evaluated by cycling the coin cells between 3.5 and 2.0 V in the temperature range of  $-30$  to  $60^\circ\text{C}$  at a current density of  $0.5 \text{ mA cm}^{-2}$  unless otherwise mentioned. The safety characteristics of the  $\text{LiV}_3\text{O}_8$  cathodes were assessed by opening the cycled coin cells in the charged (delithiated) state, washing the cathodes with propylene carbonate to remove the  $\text{LiPF}_6$  salt, hermetically sealing by crimping in an aluminum cup, and examining by a Perkin-Elmer series 7 differential scanning calorimeter (DSC) in a flowing

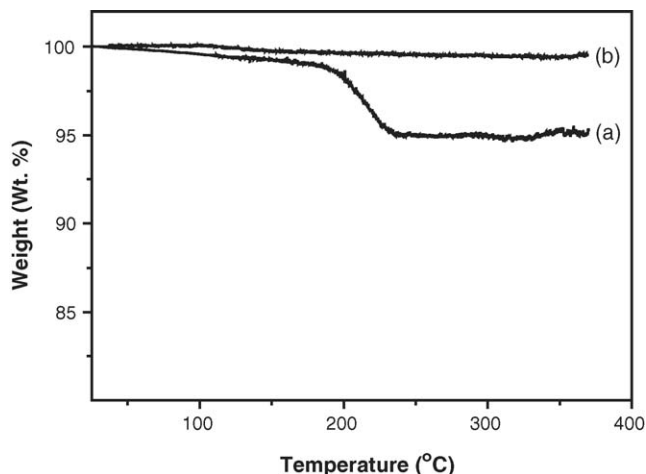


Fig. 1. TGA plots of the (a) precursor obtained by dispersing ammonium metavanadate and lithium hydroxide in methanol and (b) after heating the precursor in nitrogen atmosphere at 500 °C. The plots were recorded in  $\text{N}_2$  atmosphere with a heating rate of  $2^\circ\text{C min}^{-1}$ .

nitrogen atmosphere at a heating rate of  $10^\circ\text{C min}^{-1}$  between 50 and 450 °C.

## 3. Results and discussion

Fig. 1 shows the TGA plots of the precursor prepared with the solution dispersion method and the corresponding heat-treated (500 °C)  $\text{LiV}_3\text{O}_8$  sample. While the precursor sample shows a weight loss of about 5% around 200 °C, the heat-treated  $\text{LiV}_3\text{O}_8$  sample exhibits  $<0.5\%$  weight loss, indicating the completeness of the decomposition of the precursor during the heat-treatment at 500 °C. Fig. 2 shows the SEM photograph of the  $\text{LiV}_3\text{O}_8$  sample synthesized by the solution dispersion method, and it has a larger particle size of about  $4 \mu\text{m}$ . X-ray diffraction indicated the samples prepared by both the methods to be single phase without any impurity phases.

Fig. 3 shows the typical discharge–charge profiles of the  $\text{LiV}_3\text{O}_8$  cathode synthesized by the solution dispersion method

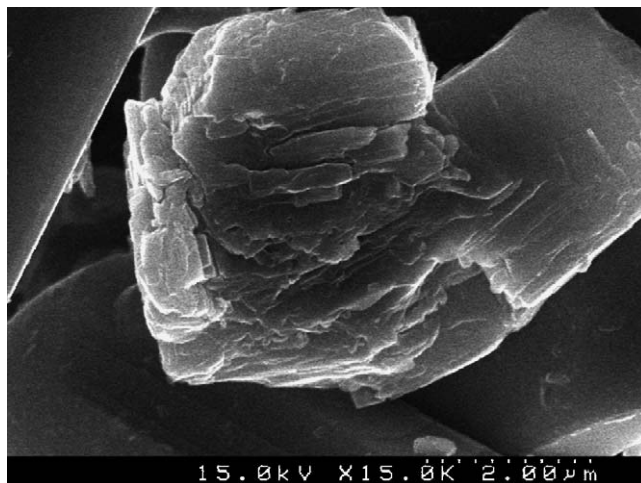


Fig. 2. SEM micrograph of  $\text{LiV}_3\text{O}_8$  synthesized by the solution dispersion method.

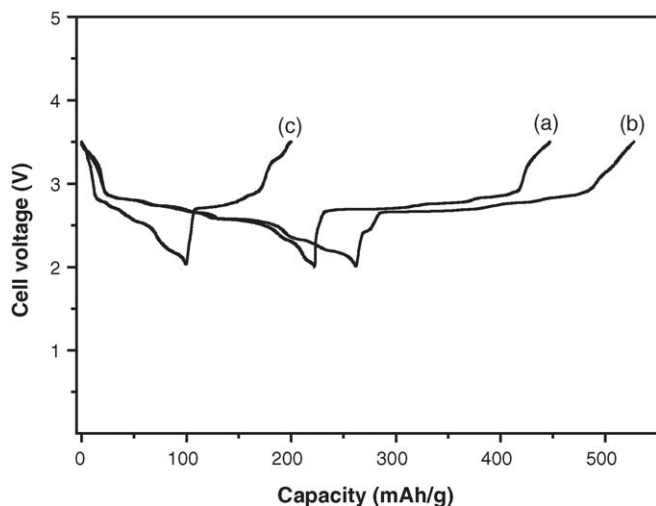


Fig. 3. Discharge-charge voltage profiles of  $\text{LiV}_3\text{O}_8$  (synthesized by the solution dispersion method) at (a)  $25^\circ\text{C}$  at  $0.5\text{ mA cm}^{-2}$ , (b)  $60^\circ\text{C}$  at  $0.5\text{ mA cm}^{-2}$  and (c)  $-30^\circ\text{C}$  at  $0.05\text{ mA cm}^{-2}$  between 3.5 and 2.0 V.

at  $0.5\text{ mA cm}^{-2}$  in the voltage range of 2.0–3.5 V at room temperature and  $60^\circ\text{C}$ . Interestingly,  $\text{LiV}_3\text{O}_8$  exhibits nearly a flat discharge profile around 2.7 V, offering a reversible capacity of around  $230\text{ mAh g}^{-1}$  at room temperature and  $260\text{ mAh g}^{-1}$  at  $60^\circ\text{C}$ . It is noteworthy to compare this voltage profile with that reported by Liu et al. between 1.5 and 4.0 V that exhibited a continuous variation of discharge voltage from 2.8 to 1.5 V [17]. In addition, Fig. 3 compares the discharge-charge profiles at  $-30^\circ\text{C}$  at a current density of  $0.05\text{ mA cm}^{-2}$ . The lower capacity at  $-30^\circ\text{C}$  is due to the limited lithium ion conductivity of the electrolyte and the cathode as well as the higher internal resistance of the cell at lower temperatures.

Fig. 4 compares the cyclability data at various temperatures of the  $\text{LiV}_3\text{O}_8$  cathodes prepared by the two methods. The sample prepared by the solid state method shows a reversible capacity of  $220\text{ mAh g}^{-1}$  (at  $0.5\text{ mA cm}^{-2}$ ) at room temperature while that

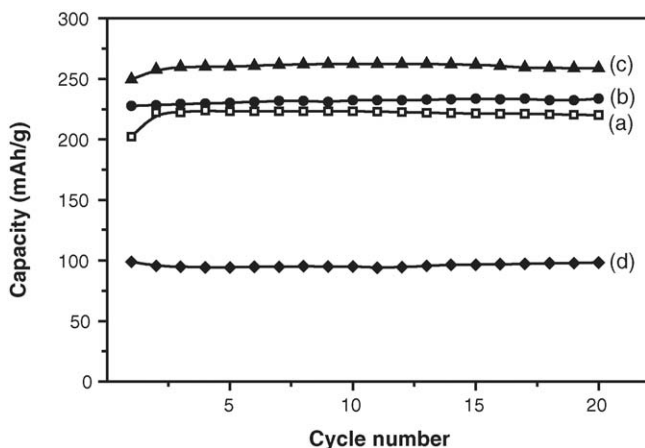


Fig. 4. Cyclability data of (a)  $\text{LiV}_3\text{O}_8$  prepared by the solid state method at  $0.5\text{ mA cm}^{-2}$  at room temperature, (b)  $\text{LiV}_3\text{O}_8$  synthesized by the solution dispersion method at  $0.5\text{ mA cm}^{-2}$  at room temperature, (c)  $\text{LiV}_3\text{O}_8$  synthesized by the solution dispersion method at  $0.5\text{ mA cm}^{-2}$  at  $60^\circ\text{C}$  and (d)  $\text{LiV}_3\text{O}_8$  synthesized by the solution dispersion method at  $0.05\text{ mA cm}^{-2}$  at  $-30^\circ\text{C}$ .

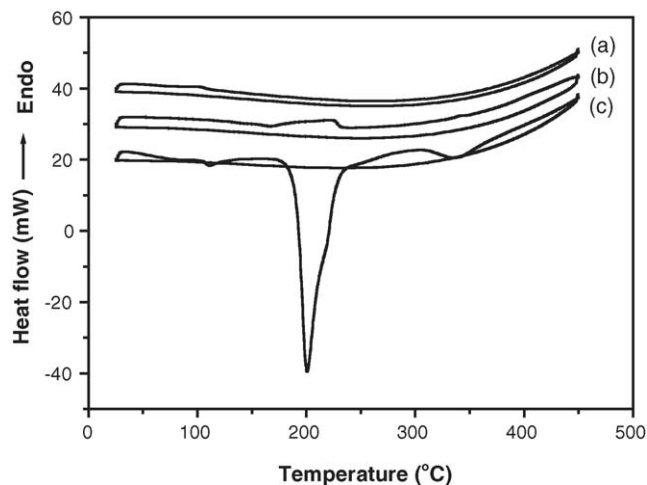


Fig. 5. DSC plots of (a) as-prepared  $\text{LiV}_3\text{O}_8$  (solution dispersion method), (b) cycled  $\text{LiV}_3\text{O}_8$  (solution dispersion method) cathode after 20 cycles in the charged state and (c)  $\text{LiCoO}_2$  cathode in the charged state.

prepared by the solution dispersion method shows a reversible capacity of  $230$  and  $260\text{ mAh g}^{-1}$  (at  $0.5\text{ mA cm}^{-2}$ ), respectively, at room temperature and  $60^\circ\text{C}$  with excellent cyclability with an average discharge voltage of 2.7 V. Although the discharge voltage is lower, the energy density value of  $\text{LiV}_3\text{O}_8$  is about 10% more than that found with the  $\text{LiCoO}_2$  cathode. Fig. 4 also shows the cyclability of the sample prepared by the solution dispersion method at  $0.05\text{ mA cm}^{-2}$  at  $-30^\circ\text{C}$ . A reversible capacity value of close to  $100\text{ mAh g}^{-1}$  could be realized at  $-30^\circ\text{C}$  with excellent capacity retention.

Fig. 5 compares the DSC plots of the as-prepared and cycled (after 20 cycles)  $\text{LiV}_3\text{O}_8$  cathodes (synthesized by the solution dispersion method) in the charged state. Fig. 5 also gives the DSC plot of  $\text{LiCoO}_2$  cathode in the charged state for a comparison. Interestingly, both the as-prepared and the cycled  $\text{LiV}_3\text{O}_8$  (charged state) cathodes do not show any exothermic peak up to  $450^\circ\text{C}$ , indicating its excellent chemical stability and safety characteristics. In contrast, charged  $\text{LiCoO}_2$  cathode shows a huge exothermic peak around  $200^\circ\text{C}$ . It is clear that  $\text{LiV}_3\text{O}_8$  does not suffer from safety concerns unlike the well-known  $\text{LiCoO}_2$  cathode. The superior safety characteristics of the  $\text{LiV}_3\text{O}_8$  cathode results from the location of the  $\text{V}^{3+/4+}:3d$  or  $\text{V}^{4+/5+}:3d$  band well above the  $\text{O}^{2-}:2p$  band unlike in the case of cobalt and nickel oxides where the  $\text{Co}^{3+/4+}:3d$  and the  $\text{Ni}^{3+/4+}:3d$  bands either overlap with or lie close to the top of the  $\text{O}^{2-}:2p$  band [23,24]. Additionally, the ready accessibility of multiple valences (5+, 4+, 3+ and possibly 2+) with vanadium has the possibility of not only offering higher capacity, but also minimizing the problems associated with over-charge or over-discharge.

Although the  $\text{LiV}_3\text{O}_8$  cathodes offer several advantages, such as higher capacity, excellent cyclability and better safety characteristics, the drawback with them at the present time is that they need lithium-containing anodes in order to be employed as cathodes in lithium-ion cells. Successful development of alternative anodes can make the vanadium oxide cathodes commercially viable for lithium ion cells.

#### 4. Conclusions

LiV<sub>3</sub>O<sub>8</sub> cathodes synthesized by simple low temperature methods exhibit a reversible capacity of around 230 and 260 mAh g<sup>-1</sup> at, respectively, room temperature and 60 °C at a high current density of 0.5 mA cm<sup>-2</sup> and a relatively narrow voltage range of 2–3.5 V. They also exhibit 100 mAh g<sup>-1</sup> at –30 °C at 0.05 mA cm<sup>-2</sup>. More importantly, the LiV<sub>3</sub>O<sub>8</sub> cathode shows superior safety characteristics compared to the LiCoO<sub>2</sub> cathode as the V<sup>3+/4+</sup>:3d or V<sup>4+/5+</sup>:3d band lie well above the O<sup>2-</sup>:2p band. Although LiV<sub>3</sub>O<sub>8</sub> may not be suitable for lithium-ion cells with the currently used carbon anodes as it does not contain extractable lithium, the lower discharge voltage range (2–3.5 V) makes it attractive for polymer electrolyte batteries from an electrochemical stability point of view. It may also be attractive for thin film solid state batteries made with metallic lithium anode.

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