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Soft-combustion synthesis of a new cathode-active material, LiVWO_6 , for lithium-ion batteries

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Abstract

Brannerite- LiVWO_6 , has been synthesized by employing a wet-chemical soft-combustion (low temperature) technique and its battery-active character as candidate cathode material in lithium-containing batteries is reported in the light of electrochemical means. Structural and thermal properties have also been studied by means of classical techniques such as XRD and thermal analysis. The structural features are found to be similar to its analogous counterpart, brannerite- LiVMoO_6 previously reported. Quasi-layered type LiVWO_6 crystallizes in brannerite structure of AB_2O_6 type, having a general formula $\text{LiM}'_2\text{O}_6$ ($\text{M}' = \text{transition metal}$) with lattice parameters $a = 9.347 \text{ \AA}$, $b = 3.670 \text{ \AA}$, $c = 6.593 \text{ \AA}$ and $\beta = 111^\circ 50'$. The thermochemical reactions that occur during the soft-combustion of the precursor mass facilitate the formation of the above compound at 434°C as deduced from TG–DTA scan. The product (LiVWO_6) thus prepared (calcined at 700°C) exhibits the submicrometer grains ($<1 \mu\text{m}$) whose specific surface area is found to be $4.97 \text{ m}^2/\text{g}$ as deduced from BET analysis. The redox behavior of the above compound has been examined for $\text{LiVWO}_6/\text{Li}^+/\text{Li}$ under the wet electrolyte (1 M LiPF_6 : EC + DMC) environment in the voltage regime 4.0 and 1.5 V using constant current technique at a current density of $0.8 \text{ mA}/\text{cm}^2$. It has been found that the test cell containing LiVWO_6/Li couple demonstrates excellent charge–discharge behavior in the voltage regime 3.0–1.5 V and the specific capacity of $\sim 240 \text{ mAh}/\text{g}$ has been deduced from the first charge–discharge cycle in the voltage regime ~ 4.0 –1.5 V. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Transition metal oxides have been evaluated extensively in the past as cathode materials for lithium-ion cell [1]. Lithium-ion technology makes use of transition metal oxide compounds at both the anode and cathode of electrochemical cells. Candidate materials extensively investigated for positive electrodes (cathodes) include LiCoO_2 , LiNiO_2 , $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$, spinel- LiMn_2O_4 , etc. In view of several environmental factors and also in the perspective of high yield in terms of capacity as well as high voltage, newer materials are being introduced recently. Amongst, a large number of vanadium-based compounds have been studied in a search for new high voltage, high capacity cathode-active materials for lithium-containing batteries [2–4]. Recently, we reported our preliminary structural and electrochemical studies on a new material, LiVMoO_6 , successfully employed

as a cathode-active material in a lithium-containing half-cell under flooded electrolyte environment [2]. In continuation of our efforts to introduce newer materials for lithium battery applications, we report here yet another new material namely brannerite- LiVWO_6 having “quasi-layered” structure delivering a specific capacity of $250 \text{ mAh}/\text{g}$ (3.88–1.5 V) as deduced from the first discharge of a half-cell containing $\text{LiVWO}_6/\text{Li}^+/\text{Li}$.

The search for the newer materials, in terms of cost and environmental acceptance, has opened a new era in solid state materials research. In the present work, we describe a low-temperature synthesis procedure, namely soft-combustion technique to produce bulk quantities of “quasi-layered” LiVWO_6 powders. This technique offers several advantages over the conventional solid state as well as other solution-based techniques known to date. Recently, Prabaharan et al. have successfully employed this technique to synthesize brannerite- LiVMoO_6 [2], inverse spinel- LiNiVO_4 [5], spinel- LiMn_2O_4 [6] and $\text{Li}_2\text{M}'_2(\text{MoO}_4)_3$ ($\text{M}' = \text{Mn, Ni, Co}$) [7] cathode materials and found that this technique could be

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used to produce bulk quantities of battery-grade lithiated metal oxide powders with desired features, viz. phase purity, particle size, surface area, product yield, etc.

LiVWO_6 crystallizes in brannerite structure of AB_2O_6 (OAOBOBOAOBOB) type, having a general formula $\text{LiM}'_2\text{O}_6$ ($\text{M}' =$ transition metals) with lattice parameters $a = 9.347 \text{ \AA}$, $b = 3.670 \text{ \AA}$, $c = 6.593 \text{ \AA}$ and $\beta = 111^\circ 50'$ [8]. Owing to its facile structural characteristics, it is thus predicted that this material could possibly be used as an intercalation material for Li-ion battery applications. Accordingly, this paper presents the details of its synthesis procedure and demonstrate our success in employing this new material as cathode in lithium-containing half-cells.

2. Experimental

2.1. Formation of “quasi-layered” LiVWO_6 : synthesis procedure

Stoichiometric amounts of lithium nitrate, ammonium metavanadate, ammonium metatungstate were first dissolved in triple distilled water and then mixed with aqueous glycine solution ($\text{NH}_2\text{CH}_2\text{COOH}$). In our previous studies involving glycine as fuel for mild combustion reaction, we have optimized that the stoichiometric composition of glycine was twice the molar fraction of total stoichiometry of the starting materials. Upon mixing glycine, the color of the total solution was turned to orange from yellow at 50°C . The mixture solution was heated to boiling and underwent dehydration at 90°C eventually leading to a blue-black sticky paste-like substance. Throughout this process, the solution was continuously stirred to keep solution homogeneity. The paste was then allowed to dry further at around 250°C and the temperature was maintained in order to allow the dried precursor mass to decompose spontaneously. The decomposition was accompanied by a mass of small bubbles (foams) followed by the generation of combustible gases such as NO_x and NH_3 , which eventually gave rise to a brown-black powder. Further, as the process continued, the volatile combustible gases ignited as a result of the exothermic decomposition, yielding a voluminous black mass called as-prepared product. During the process of preparation, it was observed that the reaction kinetics was very slow even though the reaction mixture contained glycine as fuel. This prompted us to use the terminology, namely “soft-combustion” under mild environment. The illustration showing the stepwise preparative procedure to obtain the as-prepared product is shown in Fig. 1. A theoretical reaction, assuming complete thermal decomposition of the starting materials, may be written as

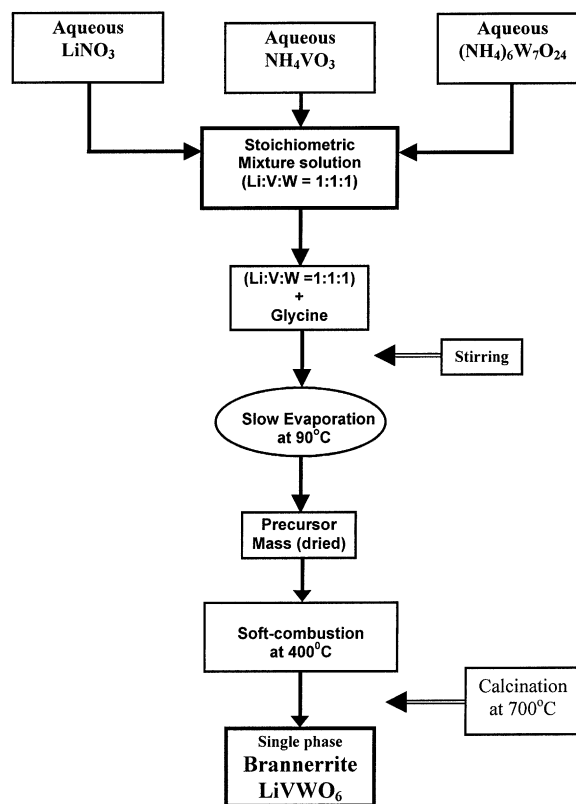
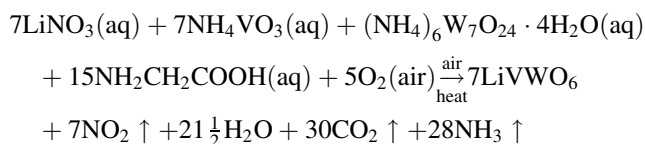


Fig. 1. Flow chart illustrating the soft-combustion process for the preparation of brannerite- LiVWO_6 .

The as-prepared product was calcined at 600 and 700°C in order to obtain well crystalline powders of the desired compound. The calcined polycrystalline powders were first examined by employing both Philips Analytical X-ray diffractometer (model PW 1830) and JEOL (model JDX 8030) X-ray diffractometer using nickel-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The diffraction patterns were taken at room temperature in the range $10^\circ < \theta < 80^\circ$ using step scans. The step size and the scan rate were set at 0.1 and $0.2^\circ/\text{min}$, respectively.

The thermal reaction mechanism such as weight loss (TG) and temperature of phase formation (DTA) of the as-prepared product (precursor) were studied using a Netzsch analyzer (model STA 409) in the temperature range from RT up to 800°C . Experiments were carried out under ambient atmosphere with a heating rate of $5^\circ\text{C}/\text{min}$.

The particle size and morphology features were collected by employing a scanning electron microscope (Cambridge Instruments, Stereoscan S200). The specific surface area (BET) analysis was carried out using Micromeritics Flow-sorb II (model 2300).

Electrochemical studies were carried out on cathodes containing LiVWO_6 powders (calcined at 700°C), black carbon and PTFE binders. The test cells were fabricated in $\text{LiVWO}_6/\text{Li}^+/\text{Li}$ two-electrode configuration following 2450 coin-type cell features. The cells were fabricated

following the procedure previously described by us [11]. Discharge tests were performed employing Arbin Instruments (Battery Testing system, BT 2000 equipped with MITS PRO software) in the potential interval, 4.0–1.5 V with a current density of 0.8 mA/cm².

3. Results and discussion

3.1. Thermal analysis

TG–DTA thermal scans display the formation temperature of the oxide product LiVWO₆ at 434°C. The huge exothermic reaction which occurred at the onset temperature (~434°C) is indicative of the total combustion of glycine and other inorganic moieties. This reaction generates an enormous amount of heat energy which presumably facilitates the oxidation–decomposition reaction under the influence of atmospheric oxygen to form the above oxide product. The mass loss of about 62.5% in the temperature regime, 90–520°C, corresponds to the removal of superficial water (due to the hygroscopic nature of the precursor), liberation of ammonia and thermal decomposition of glycine together with the decomposition of nitrates. The combustion nature of glycine together with the nitrate present in the precursor complex gave rise to enormous heat energy to ignite the total combustion of the remaining moieties in the precursor at 430°C. This indicates that the above thermal reaction provides adequate heat energy for initiating the crystallization of the final product, LiVWO₆ as indicated by the largest exothermic peak centered at ~434°C.

3.2. Phase analysis: XRD studies

The phase analysis was carried out on the synthesized product by means of powder X-ray diffraction (XRD) technique. The synthesized products were pre-heated at different temperatures with a constant soak time of 1 h in the ambient air. Fig. 2 exhibits the XRD patterns of soft-combustion derived precursor mass calcined at various temperatures. Interestingly, the pattern obtained for the as-prepared product (see Fig. 2(a)) exhibits sharp peaks indicating the high order of crystallinity together with a few undesired phases, presumably due to the presence of inorganic moieties which are left out during the soft-combustion process. However, upon calcination at elevated temperature for instance, the pattern obtained for 500 (not shown) and 600°C has still left with fewer poorly resolved residual peaks with low relative intensity as shown in Fig. 2(b). These residual peaks are found to disappear while the precursor is heated at 700°C (1 h) as evident from Fig. 2(c). It has been ascertained that the product calcined at 700°C forms the brannerite phase of LiVWO₆ as confirmed by Crystallographica Search-Match profile (Oxford Cryosystems Ltd., UK) [9]. The cell para-

meters ($a = 9.347 \text{ \AA}$, $b = 3.670 \text{ \AA}$ and $c = 6.593 \text{ \AA}$) were calculated by least-squares refinement procedure (*U-Fit software*) and the above results are well agreed with the literature [8,9]. It is interesting to note that the sharp crystalline peaks as shown in Fig. 2(c) are indicative of the presence of submicronic crystallites which is one of the desired features for the material to be considered as electrode-active material in lithium-containing batteries.

3.3. SEM/EDAX and BET analyses

In order to study the particle size distribution, shape and morphology, scanning electron microscopic (SEM) analysis was carried out for powders calcined at 550, 600 and 650°C. Fig. 3 exhibits scanning micrographs of the calcined powders of brannerite LiVWO₆. The micrographs reveal the formation of the spherical grains accompanied by controlled grain growth. The presence of loosely agglomerated spherical grains is noteworthy, the average grain size being <1 μm estimated from SEM data. As seen from the micrographs (Fig. 3), almost all the grains are well connected with linear grain boundaries and exhibit a nearly pore-free state of the calcined powders at 700°C. Nevertheless, one cannot expect the above features such as submicronic grains and pore-free state, in a similar compound prepared via conventional solid state reaction at high temperatures. The aforementioned features are very desirable for a material to be employed as electrode-active material in rechargeable lithium-containing batteries.

BET analysis provides information about the surface area of the synthesized powders. The powders calcined at 600°C (1 h) exhibits a BET area of 5.54 m²/g, which diminishes to 4.97 m²/g for the product calcined at 700°C (1 h). The latter indicates that, the surface area decreases with increasing temperature, presumably due to increased grain growth leading to nonlinear grain boundaries. The existence of these nonlinear grain boundaries would be the likely cause of the reduction in the BET surface area of the powder calcined at 700°C as evident from the SEM microstructure (not shown). But Fig. 3(c) shows the onset of such a modified grain texture. However, the physical particle size is still within submicronic level.

3.4. Electrochemical studies

Recently, Delmas et al., discussed the unique qualities of the lithium batteries in studying the new materials in the context of structural and physical properties such as the specific energy content (mAh/g), intercalation/deintercalation kinetics, redox behavior, etc. [10]. In the present work, we have deduced specific capacity of this new material as battery electrode by studying the first discharge kinetics in the test cells containing the brannerite-LiVWO₆ (calcined at 700°C) against Li⁺/Li.

As for the fabrication, the composite cathode (as positive electrode) was prepared by mixing black carbon and PTFE

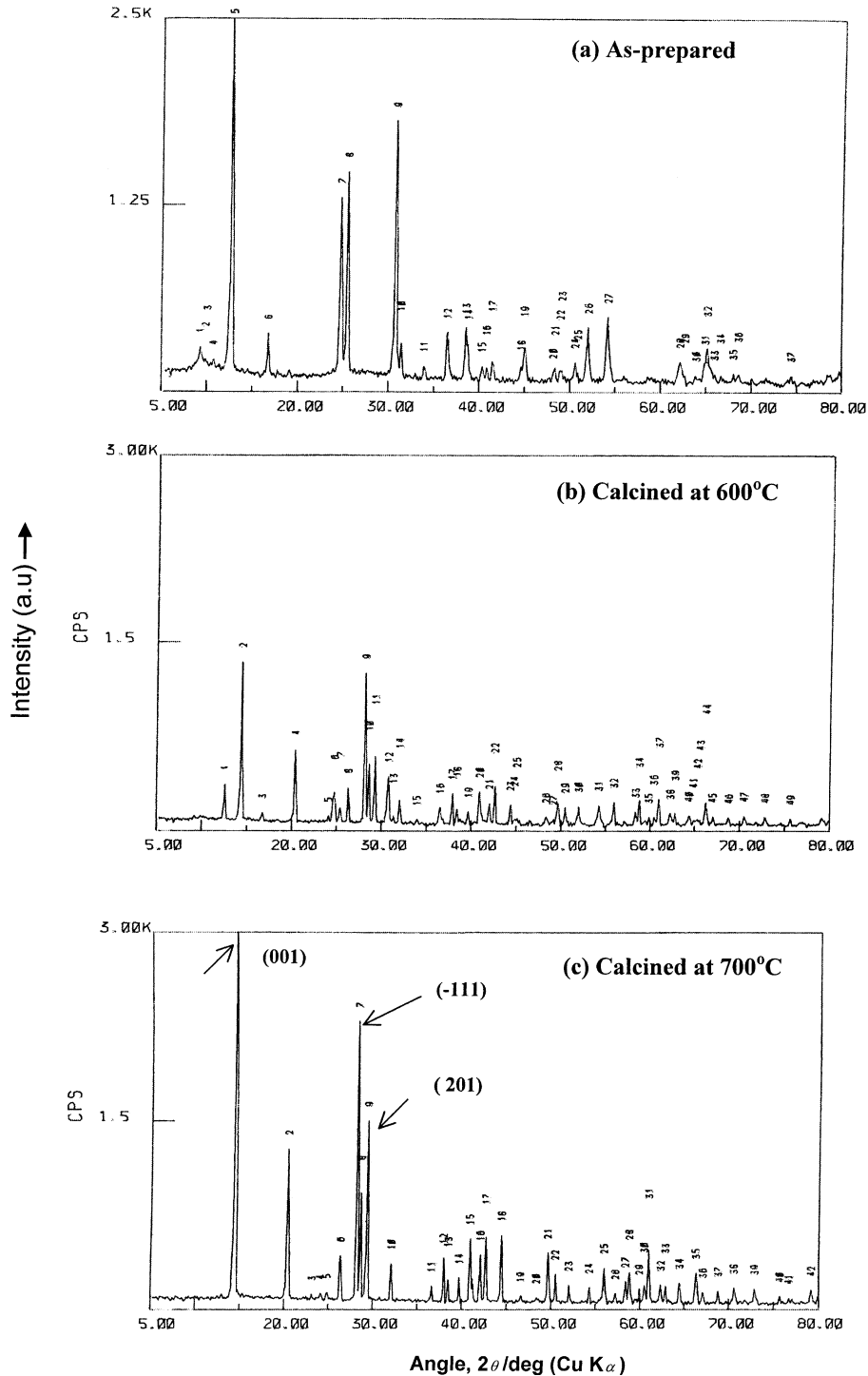


Fig. 2. X-ray diffractograms of soft-combustion derived LiVWO_6 .

binder together with LiVWO_6 powder and pressed into circular pellets incorporating a copper expanded grid mesh. The half-cells containing Li metal, liquid organic electrolyte and the composite cathode were fabricated using a Teflon-cased two-electrode cell holder designed for the purpose as described earlier [11]. The electrodes are separated by a Celgard 2400 membrane soaked in the electrolyte of 1 M

LiPF_6 in 1:1 v/v mixture of EC–DMC (LP 30, Merck). The cells thus fabricated were allowed to equilibrate under inert atmosphere until the open circuit potential (OCP) reaches a stable value (~ 4.0 V).

The galvanostatic (constant current) discharge of LiVWO_6/Li half-cell was carried out at a current density of 0.8 mA/cm^2 using Arbin Instruments battery tester

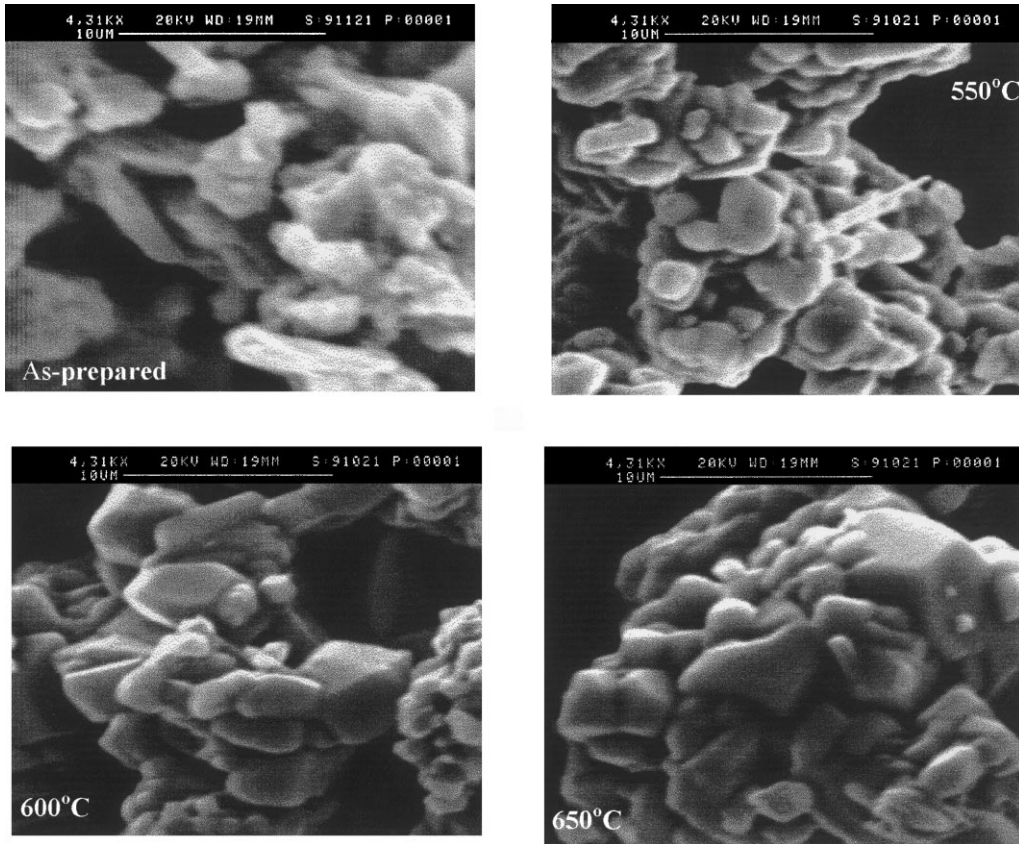


Fig. 3. SEM micrographs of the LiVWO_6 powders calcined at a different temperatures for 1 h in air.

(BT2000) and the preliminary data obtained from the first discharge is reported in this work. Fig. 4 presents the first discharge and second charge profile of LiVWO_6/Li half-cell based on the cell potential versus specific capacity (mAh/g). It is also interesting to note that the excellent flat discharge voltage profile as exemplified in terms of smooth removal of Li^+ indicates the steady state reduction kinetics of the compound. This is one of the desired features for a material

to be employed as an electrode material in practical Li-ion batteries. It is well known that the changes occurring in the cell voltage during the discharge of a lithium battery provide information on the changes in structure and physical properties induced by deintercalation processes [10]. Accordingly, Fig. 4 illustrates the smooth removal of Li^+ (deintercalation) from the host lattice (LiVWO_6) during the reduction kinetics of first discharge step. However, owing to its excellent low

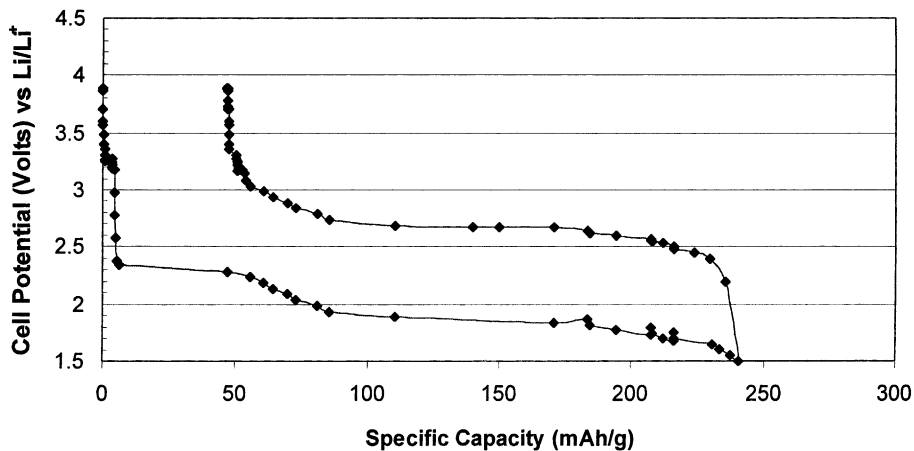


Fig. 4. Electrochemical discharge–charge profile of LiVWO_6/Li non-aqueous test. Cell; product used was calcined at 700°C .

voltage performance, this material could be listed under 3 V class category rather than high voltage class, though, the cell can be charged up to 4 V. It is note worthy that the analogous brannerite-LiVMoO₆ has been shown to yield a good high voltage profile as reported by us previously [2]. The cause for this significant change in its redox behavior of these two analogous materials is being investigated. Based on the actual weight of the active material (LiVWO₆) content included in the positive electrode, the practical utilizable capacity was calculated to be ~240 mAh/g. The preliminary electrochemical studies confirm that the layered-LiVWO₆ synthesized in the present work may be classified amongst transition metal oxide category and could be regarded as a material of choice as cathode in lithium-ion batteries. The above results encourage us to throw more light on this new cathode material for lithium battery studies. More work is underway to exploit this material as a candidate cathode material in lithium-containing cells whose complete electrochemical data is in progress and will be published elsewhere.

4. Conclusion

The present work describes the synthesis details of a new lithiated transition metal oxide (brannerite-LiVWO₆) by adopting a soft-combustion technique. It has been ascertained that this process yields submicrometer grains of battery-grade quality powders. Based on its preliminary electrochemical discharge profile obtained in actual test cells, we propose that LiVWO₆ could be considered as a material of choice for developing 3 V class Li-ion rechargeable battery technology.

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