

SYNTHESIS OF LITHIUM VANADATE AND ITS CHARACTERISATION

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In view of high specific capacity, possibility of lithium uptake to 3.0 Li/mol with respect to cycleability, structural stability, high rate capability (due to high diffusion of lithium) and deep dischargeability below 1.6 V lithium vanadate is preferred to V_6O_{13} in lithium secondary cells. To have materials of less particle size, sol-gel synthesis coupled with proper dehydration processes are followed to synthesize LiV_3O_8 and it is characterized by XRD and FTIR analysis. Results are presented in this communication.

Keywords: Lithium vanadate, sol-gel synthesis, structural stability.

INTRODUCTION

Much effort has been made in 80's to develop suitable cathode material for secondary lithium cells. TiS_2 and V_6O_{13} have been employed extensively [1]. TiS_2 had indeed impressive features in terms of reversibility and rate capability [2-3]. However, reduced energy density and instability in moist air were the main drawbacks, which limited its application in practical cells. V_6O_{13} was thought of substituting TiS_2 in lithium cells and had been tried as positive electrode [4,5]. This material has greater energy density than TiS_2 and strict stoichiometry need not be mentioned for optimum performance.

Their cycling behaviour at current densities around 1 mA/cm^2 is characterized by high and stable specific capacities after the first few cycles [6] that is 0.16-0.20 Ah/g. However, an important drawback is reported for both V_6O_{13} (stoichiometric) and especially V_6O_{13} (non-stoichiometric). At 1.6 V, a reduction process occurs which inhibited further rechargeability [6]. This is probably due to structural instability in the reorganizations connected with the high Li content ($2.37 \text{ Li}^+/\text{V}$). This drawback was the main reason to discourage the use of these materials in practical lithium cells. An attempt was made to overcome this drawback by using a material which, while retaining the basic electrochemical features of V_6O_{13} , would be able to undergo overdischarges without structural damage. The

$Li_{1+x}V_3O_8$ phase investigated in [7] is closely related in structure to V_6O_{13} .

This bronze, a layered compound whose layers are held together by Li^+ ions [7] has proven to be able to insert lithium in its structure with outstanding energy, power and cycling capability. This bronze is superior to V_6O_{13} in such aspects as energy density, rate capability, cycle life and resistance to overdischarge. On this basis this ternary oxide did seem worthy of a further investigation. Early in the development it was realized [8] that the methods used to prepare oxide strongly influenced its electrochemical properties. It was demonstrated that [8] LiV_3O_8 prepared in an amorphous glassy state by rapid quenching from the melt had a higher initial capacity than the crystalline analogue. These findings were, however, not pursued further even though several research groups reported on the use of crystalline LiV_3O_8 as host material for lithium intercalation [9- 18].

Several preparation procedures have been devised to improve the performance of LiV_3O_8 including control of stoichiometry by rapid cooling [18], more efficient grinding [19] and addition of inert nucleation centres like silica or alumina to the melt [20]. The main problem in all these seems to be that on slow cooling, LiV_3O_8 crystallized as a very hard and tough material, which is difficult to process into proper electrode structures that can maintain their integrity during deep cycling. It is recently reported that [21] fully amorphous LiV_3O_8 obtained from a precipitation technique showed significantly higher capacity, better rate

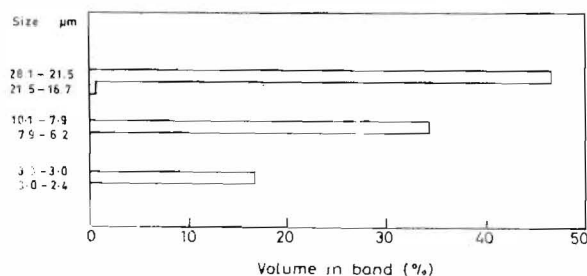


Fig. 1: Particle size analysis of LiV₃O₈

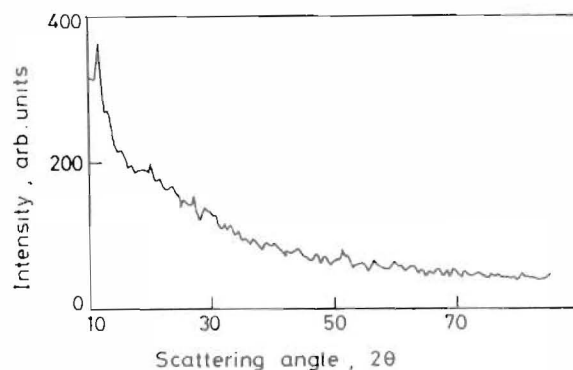


Fig.3: X-ray diffractogram of synthesised powder of LiV₃O₈

capability and longer cycle life than conventionally made crystalline LiV₃O₈.

In the present paper an adoption of sol-gel technique has been made to get materials with a controlled degree of crystallinity and a particle morphology well suited to the processing steps involved in electrode fabrication. The method is based on the dehydration of stable gels prepared from LiOH and V₂O₅ as reported in [20]. These gels are vacuum dried and further dehydrated in a heat treatment step. Powders obtained are characterized by XRD, FTIR etc.

EXPERIMENTAL

An aqueous LiV₃O₈ gel was prepared by mixing LiOH, V₂O₅ in 1:3 mole ratio. To LiOH aqueous solution V₂O₅ suspended solution was slowly added with constant stirring. The gelatinous precipitate was dried at 353 K. This powder is then vacuum dried at 393 K for 4 hours. The vacuum dried powder was then heated to 873 K for 5-6 hours to get LiV₃O₈ powder.

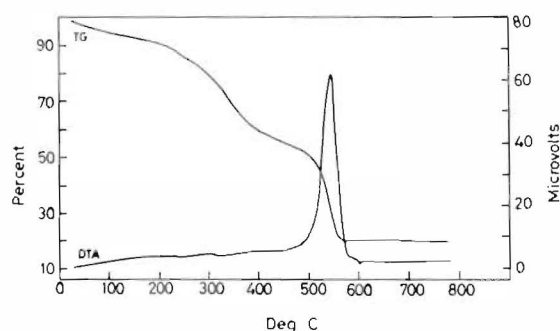


Fig.2: TG & DTA of LiV₃O₈

RESULTS AND DISCUSSION

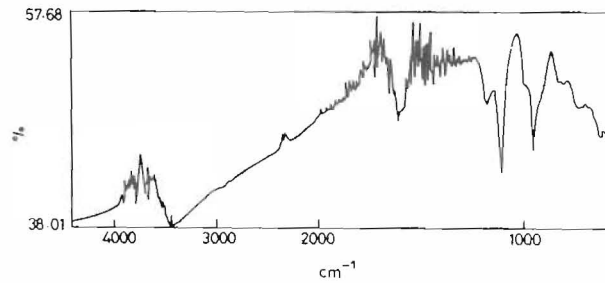
LiV₃O₈ powder synthesized is analyzed using Malvern Instruments for particle size and the result is shown in Fig. 1. Particle size is in the range of 8 to 28.1 μm. Particle size could have been reduced to still lower range if freeze drying is adopted.

From the thermogravimetric (TG) curves reported [20] it is seen that water is lost in two distinct steps below 423 to 448 K (Fig. 2). Whereas a smaller part of the water roughly corresponding to 0.5 H₂O per LiV₃O₈ unit is more strongly bound to the oxide and only released at temperatures above 473 K. Based on these observations and vacuum drying was adopted at 393 K for 4 hours. Even after drying at 873 K for 5 to 6 hours, dehydration due to water adsorption was observed and this indicates that initial drying has to be done for more hours in vacuum.

Fig. 3 shows the X-ray diffractogram of the synthesized powder of LiV₃O₈. The powder is not perfectly crystalline as it is evident from the figure and identification of the powder as LiV₃O₈ has been made from the 100% peak and it has been compared with data [22] and the unit cell parameter has been calculated and it is found to be $a = 8.132 \text{ \AA}$.

Specific resistivity was found out from I-V characteristics and it is of the order of 10³ ohm-cm and this is increased to 10⁷ ohm-cm upon lithiation done in a cell constructed using lithium vanadate as cathode, pure lithium as anode and separated by a polymer electrolyte comprising PMMA/PVC with lithium salt.

From the IR spectra as shown in Fig. 4 it is evident that the absorption bands near 1000 and 950 cm⁻¹ are associated with stretching vibration of V (2) = 0 (4) and those of V (3) = 0(7) and V (1) = 0 (5) respectively [22] where number in parentheses represents the position of the atoms labeled in [23].

Fig.4: FTIR spectra of LiV_3O_8

CONCLUSION

Lithium vanadate has been prepared by sol-gel method as this material is preferred to V_6O_{13} in lithium secondary cells due to its high cycleability, structural stability high rate capacity and deep dischargeability below 1.6 V. The material prepared by sol-gel has been characterized.

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