*Journal of Thermal Analysis, Vol. 31 (1986) 1243–1251*

# THERMAL STABILITY OF PURE AND LITHIUM INTERCALATED NON-STOICHIOMETRIC $V_6O_{13}$

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(Received October 31, 1985)

$V_6O_{13+y}$ has been prepared by thermal decomposition of $NH_4VO_3$. Lithium intercalated $Li_xV_6O_{13+y}$ ($1 \leqslant X \leqslant 6.0$) specimens have been obtained by room temperature lithiation of $V_6O_{13+y}$ with *n*-butyl lithium. Thermal stability of the compounds has been investigated by heating them in an argon atmosphere. The sequence of transformations has been studied by thermal analysis and X-ray diffraction measurements. The thermal curves of both $V_6O_{13+y}$ and $Li_xV_6O_{13+y}$ are characterized by several endo- and exothermic peaks and are quite complex in nature. Pure $V_6O_{13+y}$, on heating in an argon atmosphere, oxidizes to $V_3O_7$ and $V_2O_5$ and this is associated with a broad exothermic peak around 340 °C. The two endothermic peaks at 675 °C and 710 °C are due to the melting of $V_3O_7$ and $V_6O_{13+y}$ respectively. The compounds $Li_xV_6O_{13+y}$, on heating, partly transforms to a mixture of $\nu$-$LiV_2O_5$ and $VO_2$ accompanied by considerable oxygen loss. The extent of this conversion increases with increasing lithium content of the starting compound.

During the last few years considerable effort has been put into the search for new cathode materials for rechargeable lithium cells. In this context, different transition metal dichalcogenides as well as oxides have been thoroughly investigated by many workers [1, 2]. These compounds because of their two dimensional layered or three dimensional framework structure with adequate empty spaces can be made to undergo a topochemical type of reaction with small cations like lithium leading to the reversibility of the cells. Out of a wide range vanadium oxides between the composition limits $VO_{1.5}$ and $VO_{2.5}$ those which have been studied for this purpose are $V_2O_5$ [3–5], $V_6O_{13}$ [6–10], $VO_2(B)$ [8] etc. Among these, $V_6O_{13}$ has been paid the greatest attention because it gives the highest theoretical energy capacity of the cell. Its use as a positive electrode in lithium cells was first investigated by Murphy and coworkers in 1979 [7, 8] at Bell Labs. Later Abraham et al. [9, 11] have reported satisfactory cycling features in $LiAsF_6$–2MeTHF solutions for both stoichiometric and nonstoichiometric $V_6O_{13}$. Since then $Li/V_6O_{13}$ cells have been studied by several other groups [10, 12, 13].

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The structure of $V_6O_{13}$ may be regarded as a shear structure of $V_2O_5$ [14–16]. It contains distorted $VO_6$ octahedra joined by extensive edge sharing into both single and double zigzag chains running parallel to [010] direction. Both the single and double chains are linked by additional edge sharing into single and double sheets, respectively, both lying parallel to the (100) plane. The sheets are interleaved and joined together by corner sharing to form the three dimensional framework. The structure contains tricapped perovskite-like cavities joined through shared square faces. There are two cavities and 30 square pyramidal sites (not all equivalent) per $V_6O_{13}$ formula unit. The maximum lithium stoichiometry attainable with *n*-butyl lithium is $Li_8V_6O_{13}$ [7]. Lithium incorporation results in elongation of the unit cell in the direction of the channels.

The investigation of $V_6O_{13}$ has so far been restricted to the cells using non aqueous liquid electrolytes which are suitable for room temperature application. However its behaviour at elevated temperatures possibly in a solid state lithium battery remains unknown. The present investigation on the thermal stability of the pure and lithium intercalated $V_6O_{13}$ has been taken up with this possibility in mind.

## Experimental

Pure $V_6O_{13}$ was prepared by thermal decomposition of $NH_4VO_3$. Two different techniques were adopted for this purpose.

In the first method $NH_4VO_3$, taken in a porcelain boat, was decomposed under a steady flow (flow rate ~50 ml/min) of argon by heating up to a temperature of 400° and soaking at that temperature for different lengths of time. This was followed by heating to 450° for 2 hrs and finally at 500° for 1 hr. In the second technique, the decomposition of $NH_4VO_3$ was carried out in a specially designed long necked glass ampoule (overall length 300 mm, length of the neck 75 mm, neck diameter ~5 mm and bottom diameter 25 mm). It was heated in air at the rate of 5 deg/min upto 435°, held at that temperature for 30 min to 1 hr and finally heated to 470° for 30 min. The decomposed mass was then cooled slowly to room temperature.

The formation of $Li_xV_6O_{13}$ $(1 \leq X \leq 6)$ of different composition was accomplished by adding *n*-butyl lithium to weighed amounts of $V_6O_{13}$ kept inside an argon filled glove box. In a stoppered bottle, to a slurry of $V_6O_{13}$ in dried *n*-hexane, measured amount of *n*-butyl lithium (E. Merck, West Germany) was added dropwise with continuous stirring. The whole mixtures, after keeping for 72 hrs. in argon atmosphere, was filtered and the precipitate was washed thoroughly by dry hexane. The product was then vacuum dried at 80°. The formation of the different compounds $(Li_xV_6O_{13})$ were confirmed by X-ray diffraction measurements and the exact concentration of lithium was determined by a flame photometer (Systronics, India) as a given in Table 1.

$Li_xV_6O_{13}$ have been studied by DTA–TG and X-ray diffraction technique. Thermal analysis of the specimens were carried out in a Stanton Redcroft (U.K.) Simultaneous Thermal Analyzer (STA–780) over the temperature range of 25–750° (depending upon the composition) at a heating rate of 10 deg/min in flowing argon.

X-ray diffraction measurements were carried out in a JEOL (Model JDX 8P) diffractometer using $CuK_\alpha$ radiation.

Table 1 Exact Lithium Content in $Li_xV_6O_{13}$ determined by Chemical Analysis

| Nominal Value of $x$ | 1.0 | 2.0 | 4.0 | 6.0 |
|---|---|---|---|---|
| Observed Value of $x$ | 1.242 | 2.367 | 4.17 | 6.037 |

## Results and discussion

X-ray diffraction measurements of the products of decomposition obtained from the two techniques indicated that the glass ampoule technique produced much better result than the conventional heating under argon flow. The typical diffraction patterns of the specimens obtained by these two techniques are shown in Fig. 1. While the diffraction pattern of the specimen obtained by the ampoule technique shows only the peaks corresponding to pure $V_6O_{13}$, certain extra peaks in addition to these were obtained for the specimen prepared by the other technique. A careful examination of this pattern indicated that the latter specimen was contaminated with considerable amounts of $VO_2$(N), where $N$ stands for the normal monoclinic

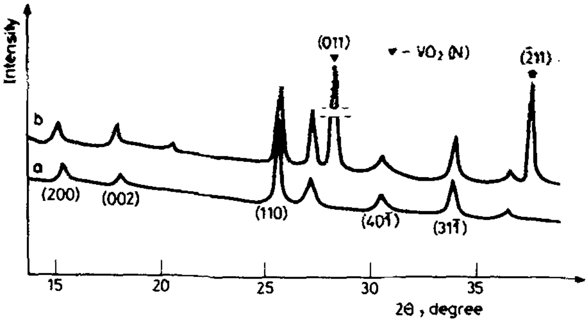

Fig. 1 Diffraction pattern of the products obtained from decomposition of $NH_4VO_3$ by. (a) glass ampoule technique; (b) argon flow method

structure. The presence of $VO_2(N)$ was also confirmed by the measurement of electrical conductivity of the pressed powders as a function of temperature. A sudden rise in conductivity was observed at around 65° which corresponded to the metal-insulator transition of $VO_2$. As expected this change in conductivity was found to be reversible with temperature. Due to this unsatisfactory result obtained with the argon flow technique, all the $V_6O_{13}$ required for the rest of the experiment were prepared by the ampoule technique. The extent of non-stoichiometry of the oxide of a particular batch which was used for the experiment was determined by measuring the weight gain of the specimen during its oxidation in air in the thermal analyzer. It was found that the material prepared was sufficiently non-stoichiometric having the exact formula $V_6O_{13.27}$.

Thermal stability of the prepared compound was investigated by DTA/TG analysis when heated in argon flow. A typical thermal curve of the compound is shown in Fig. 2. It is characterized by a broad endothermic peak associated with

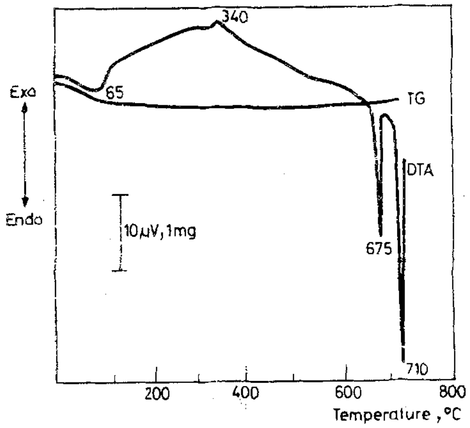

**Fig. 2** Thermal curves of pure $V_6O_{13.27}$

some weight loss below 100° indicating evaporation of physically adsorbed moisture. This is followed by a very broad exothermic effect with its peak at around 340°. The weight of the specimen remains practically constant around this temperature but slowly increases above about 400°. Finally there are two very sharp endothermic peaks at 675° and 710° which are most likely to correspond to melting of two different solid phases. X-ray analysis of the specimen heated to 500° in flowing argon shows the presence of strong diffraction peaks corresponding to $V_3O_7$ and relatively less intense peaks of $V_2O_5$ in addition to the original peaks of $V_6O_{13}$ (Fig. 3). The intensity of the $V_2O_5$ peak decreased when the specimen was heated 650°. So it is concluded that the two endothermic peaks in Fig. 2 indicate the melting of the two phases namely $V_3O_7$ at 675° and $V_6O_{13}$ at 710°. This value of

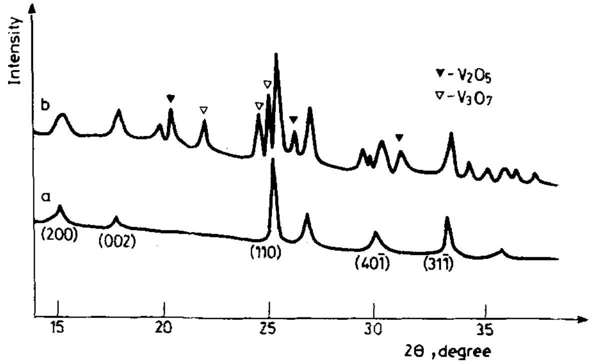

**Fig. 3** X-ray diffraction pattern of $V_6O_{13.27}$; (a) as prepared; (b) after heating to 500 °C in argon

melting point of $V_6O_{13}$ compares well with the reported value [17]. Melting of $V_2O_5$ is not detected probably due its small concentration. It may be concluded from these observations that the $V_6O_{13.27}$ prepared in this investigation was not stable upto its melting point even when it was heated in an argon atmosphere, but it partly decomposed to $V_3O_7$ and $V_2O_5$ both of which are higher oxides compared to the parent $V_6O_{13}$. However the TG results do not indicate any approciable weight gain during this decomposition probably due to the large amount of excess oxygen already present in the specimen which contributed to its non-stoichiometry.

Thermal stabilities of the lithium intercalacted specimens with different lithium concentrations were also investigated in the same manner. Thermal curves of the specimens with different lithium contents are presented in Fig. 4 (a to d). The behaviour of the $LiV_6O_{13.27}$ specimen (Fig. 4a) is very similar to that of pure $V_6O_{13.27}$ except that the melting of only one solid phase at a temperature exactly same as that of $V_6O_{13}$ is detected and there is an appreciable weight loss in the temperature range 250–450° followed by slight gain in weight above this temperature range. This weight change together with the broad exothermic peak indicates that the compound is not fully stable at elevated temperatures. On the other hand the absence of the endothermic peak at 675° suggest that $V_3O_7$ is not probably produced in this case. In fact the X-ray analysis of the specimen heated to 500° shows the presence of $\nu$-$LiV_2O_5$ and $VO_2(N)$ in addition to that of $Li_xV_6O_{13+y}$ (Fig. 5). In this case one of the decomposition products is a higher oxide while to the other one is a lower oxide and therefore there exists the possibility of oxygen loss. The following reaction may be suggested to account for the weight loss.

$$V_6O_{13} \rightarrow (1-x)V_2O_5 + (4+2x)VO_2 + x/2\ O_2 \qquad (1)$$

According to this equation higher is the percentage of $VO_2$ formed, greater will be the weight loss. It may be noted in the various thermal curves in Fig. 4 that the extent of weight loss and therefore the formation of $VO_2(N)$ increases with

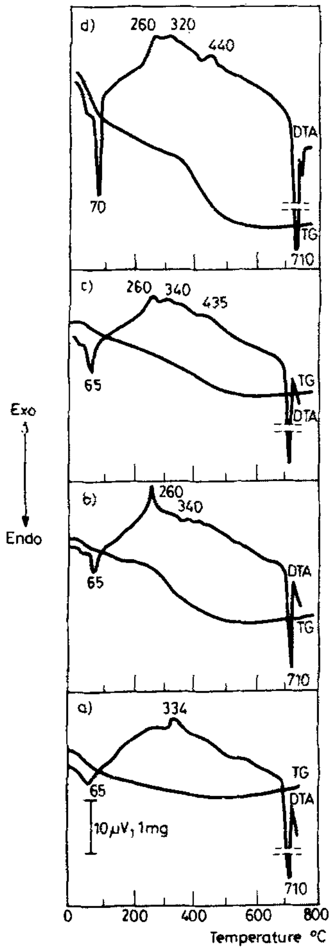

**Fig. 4** Thermal curves of $Li_xV_6O_{13.27}$; (a) $x = 1.242$; (b) $x = 2.367$; (c) $x = 4.17$; (d) $x = 6.037$

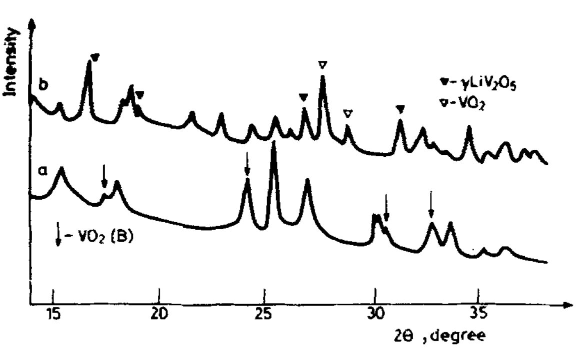

**Fig. 5** X-ray diffraction pattern of $Li_{4.17}V_6O_{13.27}$; (a) as prepared; (b) after heating to 500 °C in argon

increasing concentration of lithium in the starting compound. This is expected from the following consideration.

Stoichiometric $V_6O_{13}$ may be considered as composed of $V_2O_5$ and $VO_2$ in the form $V_2O_5 \cdot 4VO_2$. When lithium is intercalated into the $V_6O_{13}$ lattice each lithium atom is expected to donate one electron converting one of the $V^{5+}$ ions to $V^{4+}$ state. The $V_6O_{13}$ lattice is likely to be destabilized at very high concentrations of $V^{4+}$ ions with the appearance of a separate phase as $VO_2$. In fact X-ray analysis of the starting lithium inserted compounds with higher concentrations of lithium ($x > 2$) showed that these specimens were not single phase $Li_xV_6O_{13+y}$ but contained considerable amounts of $Li_xVO_2$(B) as the second phase (for example see Fig. 5). The presence of this phase is also indicated in the thermal curve by the appearance of a sharp endothermic peak at about 65° corresponding to the metal-insulator transition of $VO_2$. As expected, the intensity of the peak increases with the increasing lithium content of the starting specimen. $VO_2$(B) is structurally different than the normal $VO_2$(N) even though both of these have the monoclinic symmetry. Their lattice parameters are given in Table 2. Formation of $VO_2$(B) is usually detected when $V_2O_5$ is reduced under hydrogen flow [18]. Its structure is very close to that $V_6O_{13}$. In fact the structure of $V_6O_{13}$ may be visualized as composed of a $V_2O_5$ layer sandwitched between two $VO_2$(B) layers. It has been suggested [10] that for smaller value of $x$ in $Li_xV_6O_{13}$ the lithium ions occupy the cavities within the $V_2O_5$ layers while at higher concentration they are inserted in the cavities within the $VO_2$(B) layers. This is another possible reason for the formation of $Li_xVO_2$(B) phases at high lithium concentrations.

**Table 2** Comparison of lattice parameters of $VO_2$(B) and $VO_2$(N)

| | *a* (Å) | *b* (Å) | *c* (Å) | | Ref. |
|---|---|---|---|---|---|
| $VO_2$(B) | 12.02 | 3.693 | 6.42 | 106.6° | [18] |
| $VO_2$(N) | 5.743 | 4.517 | 5.375 | 122.6° | [19] |

Another feature of these thermal curves is that the partial decomposition of $Li_xV_6O_{13+y}$ to a mixture of $\nu$-$LiV_2O_5$ and $Li_xVO_2$ takes place over a wide temperature range (240–450°) probably in a number of distinct steps each of which is associated with an exothermmic peak. Three such peaks may be identified eventhough all of them are not clearly visible in all the thermal curves. They are better resolved for the specimens with high lithium concentration (Fig. 4b–d). These peaks appear at 260°, 340° and 440°. The exact reactions corresponding to these peaks are not known at this stage. However, one of these, possibly the one at 260°

which is not associated with significant weight change corresponds to the transformation of $VO_2$(B) to $VO_2$(N). This conversion certainly takes place during heating as the heated samples contain only $VO_2$(N).

## Conclusions

The following conclusions may be arrived at based on the present investigation.

i) The ampoule method of preparation of $V_6O_{13}$ is more suitable than argon flow method under the present circumstances.

ii) Non-stoichiometric $V_6O_{13}$ partially decomposes to $V_2O_5$ and $V_3O_7$ on heating in an argon atmosphere.

iii) $Li_xVO_2$(B) appears as second phase when $V_6O_{13.27}$ is intercalated with lithium with a concentration of more than 2Li/6V.

iv) $Li_xV_6O_{13.27}$ partly decomposes to $\nu$-$LiV_2O_5$ and $VO_2$(N) when heated above 400° in an argon atmosphere.

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The authors are grateful to Prof. A. Paul for his helpful suggestions. Partial financial support by the Electronics Commission, Govt. of India (Project No. 2/(106)/81-TDID(206)) is gratefully acknowledged.

## References

1 G. Pistoia, J. Power Sources, 9 (1983) 307.

2 K. M. Abraham, J. Power Sources, 7 (1981/82) 1.

3 J. S. Gore and C. R. Walk, J. Electrochem. Soc., 122 (1975) 68C.

4 M. R. Merriman and G. C. Vezzoli, Mater. Res. Bull., 14 (1979) 77.

5 C. R. Walk, Lithium Batteries (J. P. Gabano, ed.), Academic Press Inc. (London) Ltd. 1983. p. 265.

6 R. J. Cava and D. W. Murphy, Int. Conf. on Fast Ionic Transport in Solids, Tennessee, 1981.

7 D. W. Murphy, P. A. Christian, F. J. DiSalvo and J. N. Carides, J. Electrochem. Soc., 126 (1979) 497.

8 D. W. Murphy, P. A. Christian, F. J. DiSalvo, J. N. Carides and J. V. Waszezak, J. Electrochem. Soc., 128 (1981) 2053.

9 K. M. Abraham, J. L. Goldman and M. D. Dempsey, J. Electrochem. Soc., 128 (1981) 2493.

10 K. West, B. Zachau-Christiansen, T. Jacobsen and S. Atlung, J. Power Sources, 14 (1985) 235.

11 K. M. Abraham, J. L. Goldman and G. L. Holleck, in Proc. Symp. on Lithium Batteries, H. V. Venkatasetty (ed.), Electrochem. Soc., Princeton, N.J., 1981, p. 271.

12 B. C. H. Steele, G. E. Lagos, P. C. Spurdens, C. Forsyth and A. D. Foord, Solid State Ionics, 9&10 (1983) 391.

13 S. N. Hua and S. Phang, J. Power Sources, 10 (1983) 279.

14 K. Kawasima, K. Kosuge and S. Kachi, Chem. Lett. (1975) 1131.

15 K. A. Wihelmi, K. Waltersson and L. Kihlborg, Acta Chem. Scand., 25 (1971) 2675.

16 J. S. Anderson and B. G. Hyde, J. Phys. Chem. Solids, 28 (1967) 1393.

17 Phase diagrams for Ceramists (E. M. Levin, C. R. Robbins and H. F. McMurdie eds), The American Ceramic Society, Inc. 1964, p. 42.

18 F. Theobald, R. Cabala and J. Bernard, J. Solid State Chem., 17 (1976) 431.

19 Powder Diffraction Data File, No. 9–142.

**Zusammenfassung** — $V_6O_{13+y}$ wurde durch thermische Zersetzung von $NH_4VO_3$ hergestellt. Eingelagertes Lithium enthaltende $Li_xV_6O_{13+y}$-Proben ($1 \leqslant x \leqslant 6.0$) wurden durch Behandlung von $V_6O_{13+y}$ mit *n*-Butyl-lithium bei Raumtemperatur erhalten. Die thermische Stabilität dieser Verbindungen wurde durch Erhitzen in Argonatmosphäre ermittelt. Die aufeinanderfolgenden Umwandlungen wurden durch thermische Analyse und Röntgendiffraktometrie untersucht. Die thermischen Kurven von $V_6O_{13+y}$ sind ziemlich komplex und zeigen einige charakteristische endo- und exotherme Peaks. Reines $V_6O_{13+y}$ oxydiert sich beim Erhitzen in einer Argonatmosphäre zu $V_3O_7$ und $V_2O_5$. Dieser Prozeß geht mit einem breiten exothermen Peak bei 340° einher. Die zwei endothermen Peaks bei 675 und 710° sind dem Schmelzen von $V_3O_7$ bzw. $V_6O_{13+y}$ zuzuschreiben. Die Verbindungen $Li_xV_6O_{13+y}$ gehen beim Erhitzen unter beträchtlichem Sauerstoffverlust teilweise in ein Gemisch von ν-$LiV_2O_5$ und $VO_2$ über. Das Ausmaß dieser Umwandlung steigt mit dem Lithiumgehalt des Ausgangsmaterials an.

**Резюме** — Термическим разложением $NH_4VO_3$ было получено соединение состава $V_6O_{13+y}$. Взаимодействие этого соединения с *н*-бутиллитием при комнатной температуре приводило к внедрению лития с образованием соединений $Li_xV_6O_{13+y}$ с $1 \leqslant x \leqslant 6$. Термоустойчивость полученных соединений изучена в атмосфере аргона. Последовательность превращений была изучена с помощью термического анализа и рентгено-структурными исследованиями. Термические кривые $V_6O_{13+y}$ и $Li_xV_6O_{13+y}$ очень сложные и характеризуются несколькими эндо- и экзотермическими пиками. При нагревании в атмосфере аргона соединение $V_6O_{13+y}$ окисляется до $V_3O_7$ и $V_2O_5$, что связано с широким экзотермическим пиком около 340°. Два эндотермические пики при 675 и 710° обусловлены плавлением, соответственно, $V_3O_7$ и $V_6O_{13+y}$. Соединения $Li_xV_6O_{13+y}$ при нагревании частично превращаются до ν-$LiV_2O_5$ и $VO_2$, что сопровождается значительной потерей кислорода. Степень этого превращения увеличивается с увеличением содержания лития в исходном соединении.