

Electrical conductivity of polycrystalline lithium vanadium bronzes

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Polycrystalline lithium vanadium bronzes, $\text{Li}_x\text{V}_2\text{O}_5$ with different values of x have been prepared by both high temperature synthesis and room temperature chemical lithiation techniques. Electrical conductivity of the specimens initially increases with lithium concentration. The maximum conductivity is obtained in the β phase for the high temperature prepared specimens and in Phase II for the room temperature prepared specimens. V^{4+} concentration of the specimens has been measured by a spectrophotometric technique and its variation has been correlated with the preparation condition and conductivity.

1. Introduction

A number of transition metal oxides and chalcogenides with either two-dimensional layered or three-dimensional framework structures are found to undergo topochemical or intercalation type reactions with some guest metal ions forming a series of non-stoichiometric compounds. V_2O_5 is one such host oxide which can accommodate a number of monovalent and divalent cations, for examples sodium, lithium, potassium, silver, copper, calcium, barium etc, forming the so called "vanadium bronzes" [1]. Among these, the lithium vanadium bronzes, $\text{Li}_x\text{V}_2\text{O}_5$ ($0 < x \leq 1$), have attracted the greatest attention in recent years as possible cathode materials for high energy lithium batteries [2]. These compounds can be prepared either by high temperature (550 to 650°C) solid state reaction between suitable vanadium and lithium bearing compounds, for example V_2O_5 and Li_2CO_3 [3] or LiVO_3 , V_2O_5 and V_2O_3 [4], or by chemical or electrochemical lithiation of V_2O_5 at room temperature [5, 6]. As for many other vanadium bronzes lithium compounds prepared at high temperature exist in a series of three non-stoichiometric phases. The ranges of their homogeneity are [7] α ($0 < x \leq 0.13$), β ($0.22 \leq x \leq 0.49$) and γ ($0.88 \leq x \leq 1$). The structure of these phases and also those of analogous sodium vanadium bronzes have been studied by many investigators [8, 9]. The structure of α - $\text{Li}_x\text{V}_2\text{O}_5$ is closely related to that of the parent V_2O_5 in which the chains of edge-shared VO_5 bipyramids are linked through the corners to form a layered structure with orthorhombic symmetry. Lithium ions are inserted between the layers. The β -phase, which has been studied most widely, has a three-dimensional framework structure with monoclinic symmetry formed by a major structural rearrangement of the VO_5 bipyramids which themselves are also distorted compared to those in pure V_2O_5 . Lithium ions occupy up to a maximum 50% of the available sites in the tunnels formed by this rearrangement [1]. Further structural rearrangement occurs for the γ -phase which has once again a layered structure with orthorhombic symmetry [10].

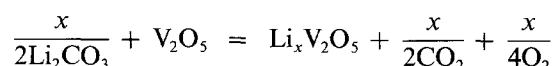
The formation of $\text{Li}_x\text{V}_2\text{O}_5$ at ambient temperature takes place with minimum structural rearrangement [5]. The three phases which have been identified in this case are designated as Phases I, II and III. Their composition limits which overlap with those of the high temperature phases are: I ($0 < x \leq 0.1$), II ($0.35 \leq x \leq 0.5$) and III ($0.9 \leq x \leq 1.0$). Phase I is isostructural with the high temperature α -phase and therefore with the parent V_2O_5 . The structures of Phases II and III are also related to the parent V_2O_5 but there are variations in the lattice parameters, and therefore, they are not related to the corresponding high temperature β - and γ -phases.

Transport properties of the most important β -phase alkali bronzes, the one-dimensional conductors, particularly that of β - $\text{Na}_x\text{V}_2\text{O}_5$ in the single crystal form have been studied extensively by various experimental techniques to ascertain its electronic structure and transport mechanism [11-14]. The electronic conductivity is highly anisotropic. Its value parallel to the b -axis is more than an order of magnitude higher than that in the perpendicular direction. However, the data on the electrical conductivity of polycrystalline $\text{Li}_x\text{V}_2\text{O}_5$ are quite limited even though they are useful for the evaluation of these compounds as cathode materials in lithium batteries.

In the present investigation a systematic study has been carried out on the electrical conductivity of different samples of $\text{Li}_x\text{V}_2\text{O}_5$ prepared by both high and ambient temperature processes and the results have been correlated with the theoretical and experimentally obtained values of V^{4+} ion concentration in the specimens.

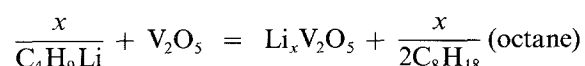
2. Experimental details

The specimens were prepared by both high temperature and room temperature processes. In the high temperature process, pure V_2O_5 and Li_2CO_3 were allowed to react according to the following equation



Required proportions of V_2O_5 and Li_2CO_3 were mixed thoroughly in an agate mortar under acetone, dried and pressed into pellets measuring 10 mm diameter and 2 to 3 mm thickness, in a steel die under a pressure of 200 MPa. The pellets were sintered at temperatures between 550 and 600°C (depending on composition) for 24 h, under sufficiently high flow rate of argon. For better homogenization the pellets were crushed, repelletized and resintered under identical conditions. This process was found satisfactory to prepare the specimens with x values up to 0.4 i.e. the specimens with α - and β -phases. However, the γ -phase could not be produced by this technique. The compositions with $x > 0.5$ produced a completely different compound namely $Li_{1+x}V_3O_8$ than the expected γ - $Li_xV_2O_5$. It was believed that the argon atmosphere maintained during sintering was not reducing enough to drive out all the excess oxygen particularly when the proportion of Li_2CO_3 was high. So, only the specimen γ - LiV_2O_5 was prepared by following a slightly different heat treatment schedule. The required mixture of Li_2CO_3 and V_2O_5 was first melted at 750°C in an argon atmosphere for 2 h and then slowly cooled to room temperature when the product obtained was $Li_{1.5}V_3O_8$. This was then finely ground and annealed at 500°C for 1 h under pure hydrogen flow to obtain the required γ - LiV_2O_5 . For electrical measurement the powders were pelletized and sintered at 500°C in hydrogen for a short time.

Low temperature preparation of $Li_xV_2O_5$ was carried out at room temperature ($\sim 28^\circ C$) by chemical lithiation of pure V_2O_5 following the method described by Dines [15] using n -butyl-lithium according to the following exothermic reaction



To a suspension of V_2O_5 in dried and distilled n -hexane, the required amount of n -butyl-lithium dissolved in n -hexane was added dropwise with constant stirring. Slight excess of n -butyl-lithium was always added to compensate for any loss. The mixture was kept for 3 days with occasional stirring before the oxide particles were filtered out. They were washed repeatedly with dry n -hexane to remove any unreacted n -butyl-lithium and finally dried at 100°C for 3 h. The complete operation was carried out inside an argon filled glove box. For electrical measurement, the dried powders were pelletized by pressing but were not sintered at high temperature to avoid any structural change.

Phase analysis of all the specimens were carried out by X-ray diffraction technique. D.c. electrical conductivity of the specimens was measured under vacuum on the pressed pellets, the flat surface of which were coated with conducting silver paste. The impressed voltage was limited to only 10 mV. Lithium concen-

TABLE I Phase analysis of the prepared specimens

x in $Li_xV_2O_5$	0.05	0.1	0.2	0.3	0.4	0.6	0.8	1.0
HT	α	α	$\alpha + \beta$	β	β	—	—	γ
RT	I	I	I + II	II	II	II	II + III	III

tration of each of the specimens was measured by a flame photometric technique after dissolving the specimens in dilute H_2SO_4 . Experimentally determined lithium concentration for each of the specimens were very close to the desired nominal compositions. The same solution was also used to determine the V^{4+} and V^{5+} concentrations in the specimens. For this purpose the optical density of the solution was measured with a spectrophotometer (Beckman Model 5270) at 760 nm which was caused by the presence of V^{4+} ions only. To measure the total vanadium content, any V^{5+} ion present in the solution was reduced to V^{4+} by adding sufficient amount of sodium sulphite and boiling off the excess SO_2 . V^{4+} concentration of this solution was determined once again by the spectrophotometric technique. The difference between the optical densities of the two solutions was a measure of V^{5+} concentration. Exact values of these concentrations were obtained from the calibration curve drawn with the help of standard solutions.

3. Results and discussions

Phase analysis of both the high temperature (HT) and room temperature (RT) prepared specimens by X-ray diffraction techniques indicated the presence of the various phases as reported by earlier investigators [1, 5] even though the composition limits were slightly different (Table I). Phase I of RT and α of HT specimens were identical. Phase I did not undergo any change on heating. However, Phases II and III were found to be metastable. On heating above 350°C in an argon atmosphere, they transformed to the different high temperature phases which did not always correspond to the phases obtained in the HT specimens of the same composition. These transformations were associated with exothermic differential thermal analysis (DTA) peaks between 300 and 350°C. The Phase II transformed to a mixture of β - $Li_xV_2O_5$ and $Li_{1+x}V_3O_8$ while Phase III to a mixture of γ - $Li_xV_2O_5$ and $Li_{1+x}V_3O_8$.

Conductivities (σ) of the different specimens were measured in the temperature range 25 to 150°C. In each case a straight line plot is obtained for $\log \sigma$ against $1/T$ as shown in Figs 1 and 2 for the two different groups of the specimens. In general the conductivities of the HT specimens are higher than those of the RT specimens. One of the reasons for this difference arises from the fact that the RT specimens for conductivity measurement were prepared only by

TABLE II Activation energy (in eV) for conduction in $Li_xV_2O_5$

x in $Li_xV_2O_5$	0.05	0.10	0.20	0.30	0.40	0.60	0.80	1.0
HT	0.155	0.142	0.073	0.055	0.035	—	—	0.358
RT	—	0.233	0.190	0.173	0.117	0.082	0.192	0.213

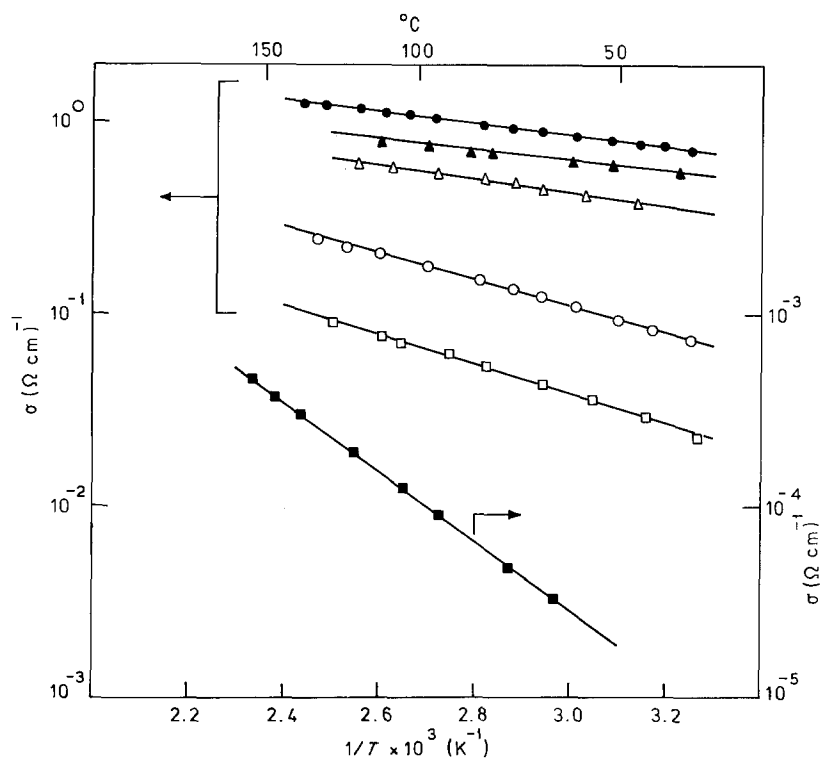


Figure 1 Temperature dependence of electrical conductivity of $\text{Li}_x\text{V}_2\text{O}_5$ prepared at high temperature. x in $\text{Li}_x\text{V}_2\text{O}_5$ (\square) 0.05, (\circ) 0.1, (\triangle) 0.2, (\blacktriangle) 0.3, (\bullet) 0.4, (\blacksquare) 1.0.

pressing the powders, they were not sintered at elevated temperatures. Accordingly the grain to grain contact was not as good as in case of HT specimens.

The activation energies calculated from these plots vary over a wide range (between 0.035 and 0.358 eV) for different specimens (Table II). Generally the higher values are obtained for the specimens with lower conductivity. Minimum activation energy of 0.035 eV is obtained with the highest conducting β -phase. This value is comparable with the values obtained for single crystal $\beta\text{-Na}_x\text{V}_2\text{O}_5$ measured at low temperature [16]. These are 0.049 eV parallel to the "b-axis" and 0.076 eV perpendicular to the "b-axis".

The conductivity of the specimens at any fixed temperature initially increases with increasing lithium concentration but decreases at higher concentrations

reaching a maximum value at some intermediate composition as shown in Fig. 3.

$\text{Li}_x\text{V}_2\text{O}_5$ as well as the parent V_2O_5 are known to be hopping semiconductors in which the electrical conduction is because of thermally activated electron transfer between V^{4+} and V^{5+} sites. The presence of V^{4+} in pure V_2O_5 is due to non-stoichiometry created by oxygen vacancies whereas the creation of V^{4+} in $\text{Li}_x\text{V}_2\text{O}_5$ is due to complete ionization of the alkali metals and trapping of the released electron at the vanadium site. Ideally pure V_2O_5 should not contain any V^{4+} ion. Each lithium atom added to the structure on ionization is likely to produce one V^{4+} ion. Accordingly, one can calculate the theoretical V^{4+} ion concentration in any of the compositions of $\text{Li}_x\text{V}_2\text{O}_5$ and there should be a linear dependence between the

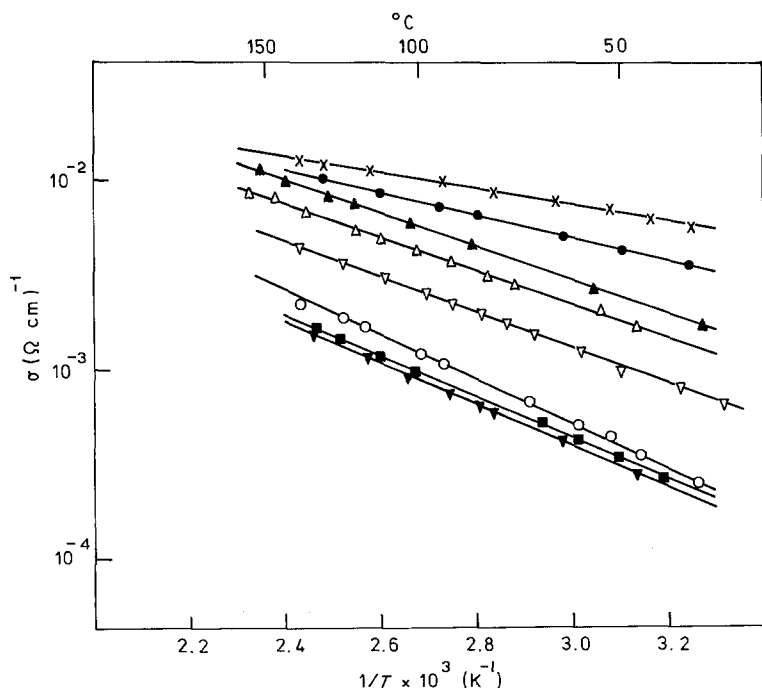


Figure 2 Temperature dependence of electrical conductivity of $\text{Li}_x\text{V}_2\text{O}_5$ prepared at room temperature. x in $\text{Li}_x\text{V}_2\text{O}_5$ (\circ) 0.1, (\triangle) 0.2, (\blacktriangle) 0.3, (\bullet) 0.4, (\times) 0.6, (∇) 0.8, (\blacksquare) 1.0, (\blacktriangledown) 1.1.

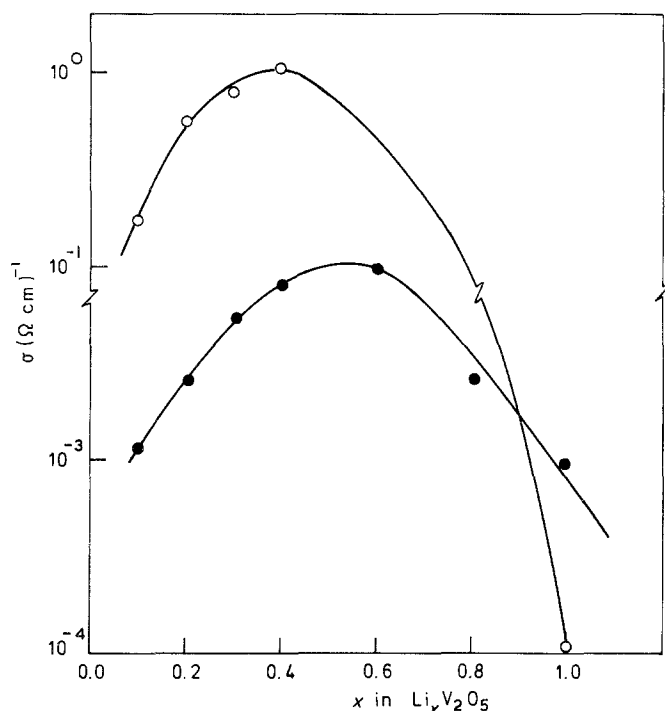


Figure 3 Variation of conductivity with x in $\text{Li}_x\text{V}_2\text{O}_5$ prepared at different conditions. (○) HT, (●) RT.

V^{4+} concentration and “ x ” as plotted in Fig. 4. This figure also includes the experimentally obtained V^{4+} concentrations of the different specimens. As expected the V^{4+} ion concentration for each set of specimens (RT and HT) increases with increasing “ x ”. For the RT specimens the variation closely follows the theoretical line except that the value at each composition is slightly more than the theoretical value. Extrapolation of this line to $x = 0$ corresponds to the V^{4+} ion concentration initially present in the pure V_2O_5 sample. It may be mentioned that the experimentally determined V^{4+} concentration in pure V_2O_5 ($\sim 2.5\%$) compares very well with the extrapolated value. In comparison to that of the RT specimens, the behaviour of the HT specimens is slightly different. Not only the variation, in this case, is non-linear but also the V^{4+} concentration at each composition, particularly at lower values of x , is much higher than the theoretical values. The only possible reason for the excess V^{4+} concentration in these specimens is the presence of appreciable

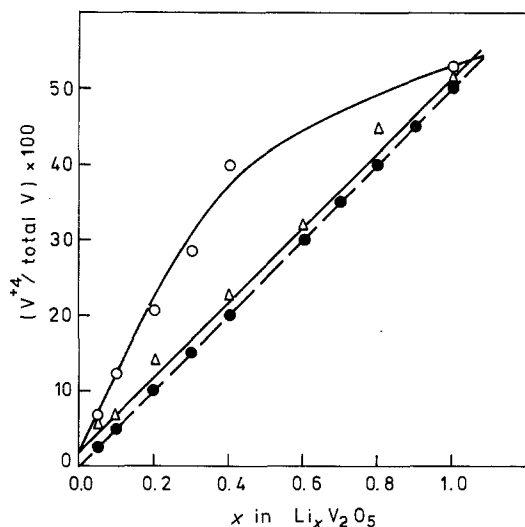


Figure 4 Variation of V^{4+} /total vanadium ratio with x in $\text{Li}_x\text{V}_2\text{O}_5$ prepared at different conditions. (○) HT, (Δ) RT, (●) calculated.

quantities of oxygen vacancies which are also responsible for the conversion of V^{5+} to V^{4+} . Creation of these excess oxygen vacancies was not possible during room temperature lithiation and so the V^{4+} concentration in the RT specimens exactly coincided with the theoretically expected values. The HT specimens were not only sintered at elevated temperatures, but also a relatively reducing atmosphere was maintained during sintering. These conditions were favourable for the creation of excess oxygen vacancies. The maximum deviation from the theoretical line occurs at a composition of around $x = 0.4$ even though identical atmosphere and temperature of sintering were used for all the compositions except $x = 1.0$. For this highest composition it is also interesting to note that the experimental V^{4+} concentration almost coincides with the theoretical value even though the specimen was annealed under a relatively more reducing atmosphere (pure H_2). These observations suggest that it is easier to create oxygen vacancies in the β -phase probably due to its relatively more open structure than in either α - or the γ -phase. This conclusion is also supported by the fact that a strongly reducing atmosphere was required to prepare the γ - $\text{Li}_x\text{V}_2\text{O}_5$ phase, otherwise, the formation of a higher oxide $\text{Li}_{1+x}\text{V}_3\text{O}_8$ resulted.

As in the case of single crystal vanadium bronzes, for these polycrystalline specimens also the β -phase shows the highest conductivity. The conductivity of the γ -phase is considerably lower even though its V^{4+} concentration is higher than that of the β -phase. This may be attributed to either or both of the following reasons: (a) the electronic mobility in the γ -phase is considerably lower than that in the β -phase, (b) as for the β -phase [16] only a fraction of the V^{4+} sites in the γ -phase contributes to the hopping conduction.

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