Structure and properties of lithium trivanadate—a potential electroactive material for a positive electrode of secondary storage

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Abstract

Quantum-chemistry calculations were carried out to predict not only the structure, but also the energetic and electrical parameters of lithium trivanadates of the formulae $Li_{1+x}V_3O_8$ (where $x = 1, 2$ and 3). Altogether 21 entities were considered: four with the formula LiV_3O_8, 14 with the formula $Li_2V_3O_8$ two with the formula $Li_3V_3O_8$ and one with the formula $Li_4V_3O_8$. A lithium–vanadium bronze with the formula $Li_{1.3}V_3O_8$ was synthesised and investigated in order to compare experimental and predicted characteristics. The presence of $Li_{1+x}V_3O_8$ units in the synthesised material was confirmed by infrared (IR) measurements. The predicted value of the open circuit voltage (OCV) change for the insertion of one lithium atom equal to 0.559 V compares well with the experimental value of 0.52 V for the insertion of the first lithium atom into the synthesised bronze. These results form the basis for predicting the properties and modelling or technologically interesting electroactive materials. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Lithium trivanadate (bronze); Insertion of lithium; Quantum-chemistry calculations; Structure; Energetic and electrical parameters

1. Introduction

More than 20 years have passed since the lithium–vanadium bronze ($Li_{1+x}V_3O_8$) was used as an alternative to V_6O_{13} cathode material in secondary lithium cells [1]. The crystalline $Li_{1.1}V_3O_8$ is monoclinic and belongs to the $P2_1/m$ space group. It is composed of two basic structural units, namely, a VO_6 octahedron and a VO_5 distorted trigonal bipyramids [2].

It was found that the electrical properties of $Li_{1+x}V_3O_8$, such as discharge capacity, discharge rate and reversibility and cyclability, depend on the method of synthesis of the compound and the conditions under which the cathode is prepared. Several methods of production and processing $Li_{1+x}V_3O_8$ electrodes, have been reported they are based on: fast cooling [3], hydrothermal treatment [4], substitution of lithium with other monovalent cations, (like Na^+ or K^+) [5], dehydration of the lithium vanadate aqueous gel [6], intercalation of inorganic molecules (NH_3, H_2O, CO_2) into the interlayer [7], ultrasonic treatment [8].

The electrochemical properties and insertional abilities of $Li_{1+x}V_3O_8$ cathode depend on their structure. It is known

that amorphous bronzes have higher discharge capacity than crystalline ones [9]. Kawakita et al. have confirmed earlier reports that the insertion rate of the lithium ions depends strongly on the degree of crystallinity of the material [10]. The electrochemical and physico-chemical properties of this compound have also been studied by other researchers using EPR, [7]Li nuclear magnetic resonance, as well as infrared (IR) and Raman spectroscopies [11–13].

Application of quantum and statistical mechanics becomes an useful tool in predicting the structure and electrochemical properties of electroactive materials. So, the value of open circuit voltage (OCV) changes for the lithium–MnO_2 (spinel or globular) cell was predicted at the ab initio level using a pseudopotential [14]. With method, the Gibbs free energy changes accompanying $Li_{1+x}CoO_2$ formation were calculated for different number of Li^+-ions in the host structure [15]. Computer simulation methods were used to analyse the initial stages of Li^+ migration across the V_2O_5/Li_2SiO_3 phase boundary [16]. The local-density functional theory was also used to study the structure and phase transitions of the monoclinic $Li_{1+x}V_3O_8$ [17].

In this work, we show how the ZINDO quantum chemistry method can be used to model the structure of lithium trivanadate and predict its electrical and energetic parameters. We further demonstrate how the predicted

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chracteristics compare with the experimentally determined structural (IR) and electrical (coulometric titration) characteristics of this electroactive material.

2. Experimental

The lithium–vanadium bronze was prepared hydrothermally from LiOH and V_2O_5 at a temperature of about 50 °C, according to the method described in the literature [9]. The synthesised bronze was washed several times, first with distilled water, then with methanol, after which it was vacuum dried at 150 °C for 24 h. The cathode was a mixture of the lithium trivanadate thus obtained, an electroconducting additive, and PTFE powder in the weight ratio 3:2:1, ABG-74 expanded graphite (Superior Grafite Company, USA) or TA-80 acetylene soot (USSR) served as electroconducting additives. After the addition of acetone, the mixture of the above three components was kept in suspension for 2 h and subjected to ultrasonic treatment for 1.5 min. After evaporation of the acetone, the mixture was vacuum dried at 200 °C for 24 h and subsequently pressed, at a pressure of 5 MPa, into a nickel net. Prismatic cells were then produced in which the cathode was the one described above and the anode was lithium foil.

The content of the lithium ions intercalated into $Li_{1+x}V_3O_8$ was determined by coulometric titration at a current of 300 μA applied for 300 s as described before [18]. IR spectra of $Li_{1+x}V_3O_8$ dispersed in KBr (4000–400 cm^{-1} region) or polyethylene (500–100 cm^{-1}), were recorded using a Bruker IFS 66 FTIR instrument with resolution varying between 1–4 cm^{-1}.
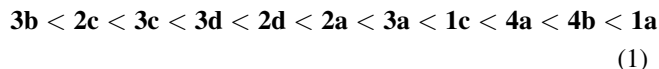
3. Computational procedure

The structure and physico-chemical characteristics of the lithium trivanadates were predicted at the level of the ZINDO semi-empirical quantum chemical method [19] included in the HYPERCHEM program package [20]. The 21 most probable and energetically favourable entities originating from $Li_{1+x}V_3O_8$ were initially optimised using molecular mechanics. These structures were then subjected to full quantum-mechanical calculations in order to obtain final characteristics.

4. Results and discussion

Fig. 1 depicts four different entities of formula LiV_3O_8 containing pentavalent vanadium, which represent the classical views of the bonding of elements. From the chemical point of view, the lithiation of LiV_3O_8 involves the electrochemical reduction of vanadium: the insertion of the first lithium atom, leads to the reduction of one vanadium atom from +5 to +4, insertion of the second lithium atom leads to the reduction of the next vanadium atom; and so on. Pentavalent vanadium exists in the singlet state, whilst the quadrivalent vanadium is in the doublet state. Therefore, during the intercalation of one, two, and three lithium atoms the multiplicity of the lithiated bronze changes to doublet, triplet and quartet, respectively. In consequence, the number of possible forms increases substantially: at least 14 entities of formula $Li_2V_3O_8$ should be considered (Fig. 2).

The initial stage of lithium insertion into LiV_3O_8 was investigated experimentally and the analysis indicated which $Li_2V_3O_8$ forms are most favourable. In the case of higher lithiated bronzes $Li_{1+x}V_3O_8$ (where $x = 2$ and 3), only three forms were taken into consideration (Fig. 3).

The bond energy of a compound (E_{bin}) can be considered a criterion of its stability. (E_{bin}) is the difference between the energy of the compound and the energy of two atoms at absolute zero. According to the molecular orbital theory, the bonding of two atoms takes place when electrons move from the atomic orbitals to the bonding molecular orbital which is accompanied by an decrease in energy [21]. If this energy decrease does not occur, a molecule is not formed, as in the case of **2b** and **4c**. On the other hand, the most stable entity is **3b**, for which $E_{bin} = -2182.1$ KJ/mol. Other possible forms of $Li_2V_2O_8$ can be arranged as shown below, in decreasing order of bond energy:

$$\textbf{3b} < \textbf{2c} < \textbf{3c} < \textbf{3d} < \textbf{2d} < \textbf{2a} < \textbf{3a} < \textbf{1c} < \textbf{4a} < \textbf{4b} < \textbf{1a} \tag{1}$$

Doubly lithiated bronze can exist in the two forms **5a** and **5b** presented in Fig. 3, the multiplicity of which is 3. However, according to quantum chemical calculations, only **5b** is stable.

In the case of trilithiated bronze the vanadium atoms can all be quadrivalent only in structure **6**. Therefore, the
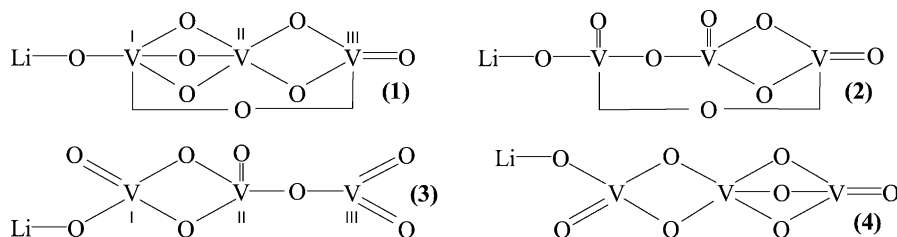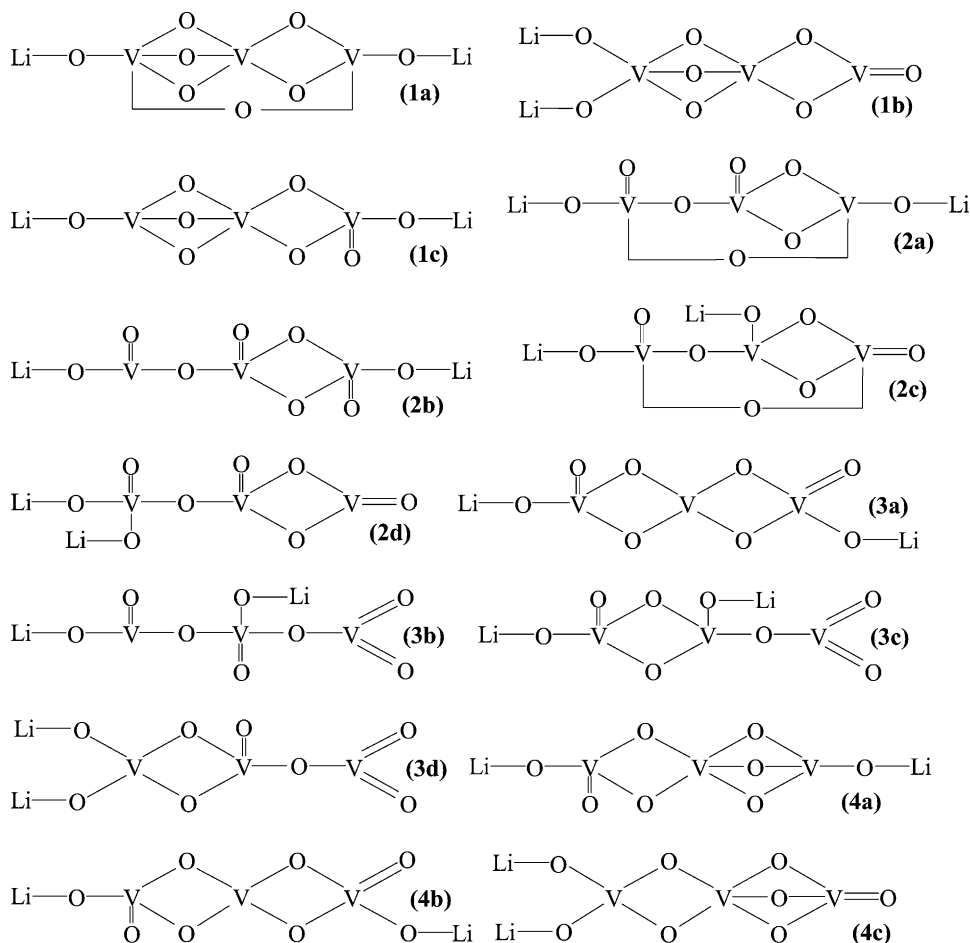

Fig. 1. Possible structures formulae of LiV_3O_8.

Fig. 2. The structural formulae of the monolithiated bronze ($Li_2V_3O_8$).

lithiation process can be presented as a transition between the following forms of the bronze

$$1 \rightarrow 1a \rightarrow 5b \rightarrow 6 \qquad (2)$$

The energetic characteristics and relative charges on selected atoms for some of the compounds are listed in the Table 1. The increase in the number of inserted lithium atoms causes a decrease in the energy of the lowest unoccupied molecular orbital (E_{LUMO}). This indicates that with the increase in the degree of lithiation, the susceptibility of the bronze to reduction increases. On the other hand, there is no correlation between the degree of lithiation and the ΔE_q ($E_{LUMO} - E_{HOMO}$) gap, or the relative charges on lithium or the relative charges on lithium or vanadium atoms.

The enthalpy change for bronze lithiation is roughly equal to the Gibbs free energy change (ΔG_r) since the entropy change for this process is insignificant and can be neglected [14].

The OCV changes for lithium insertion (ΔE) can be calculated from the Gibbs free energy changes in accordance with the equation,

$$\Delta E = \frac{-\Delta G_r}{(x_2 - x_1)F} \qquad (3)$$

in which ($x_2 - x_1$) denotes the stoichiometric coefficient for the intercalation of Li^+ into the bronze cathode; and F is the Faraday's constant. Table 2 sets out the Gibbs free energy
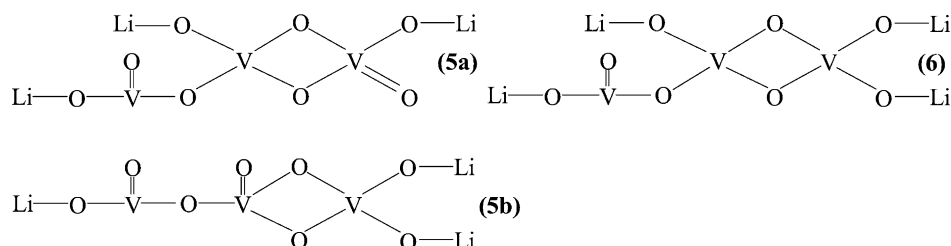

Fig. 3. The structural formulae of the bilithiated ($Li_3V_3O_8$) and trilithiated ($Li_4V_3O_8$) bronzes.

Table 1
Energetic characteristics and relative charges on atoms in $Li_{1+x}V_3O_8$

Compound (formulae no.)	E_{bin} (kJ $\times$ mol^{-1})	ΔH_f (kJ $\times$ mol^{-1})	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE_q (eV)	Relative Mulliken charges						
						V(I)	V(II)	V(III)	Li(I)	Li(II)	Li(III)	Li(IV)
LiV_3O_8 (**1**)	−345.8	3353.5	−7.355	0.228	7.583	0.53	0.66	0.80	0.39			
$Li_2V_3O_8$ (**1a**)	−560.7	3299.5	−6.410	0.195	6.605	0.69	0.84	0.49	0.23	0.40		
$Li_3V_3O_8$ (**5b**)	−666.5	3352.9	−9.881	−0.760	9.121	0.82	0.73	1.04	−0.42	−0.12	−0.07	
$Li_4V_3O_8$ (**6**)	−720.6	3457.8	−8.930	−1.042	7.888	0.88	0.50	1.07	−0.33	0.30	0.50	−0.24

Table 2
Gibbs free changes and OCV value for the intercalation of Li^+ ions

Intercalation process	ΔG (kJ $\times$ mol^{-1})	E (V)
$LiV_3O_8 + Li^+ + e \rightarrow Li_2V_3O_8$	−54.00	0.559
$Li_2V_3O_8 + Li^+ + e \rightarrow Li_3V_3O_8$	53.35	−0.552
$Li_3V_3O_8 + Li^+ + e \rightarrow Li_4V_3O_8$	104.85	−1.086

changes and the OCV changed corresponding to the insertion of one two, and three Li atoms as calculated by quantum chemical methods.

Clearly, the value of ΔG_r for the intercalations, of the first Li^+ into the bronze cathode, and F is the Faraday constant. Table 2 sets out the Gibbs free energy changes and the OCV and changes corresponding to the insertion of one, two, and three Li atoms as calculated by quantum chemical methods.

Clearly, the value of ΔG_r for the intercalation of the first Li^+ is negative, which means that the process is thermodynamically favourable and should proceed spontaneously. On the other hand, intercalation of the second and third lithium atoms is a forced process. Intercalation of lithium into the synthesised lithium–vanadium bronze ($0 < x < 1$) was investigated by coulometric titration (Fig. 4). The OCV changes versus x were measured for electrodes containing either expanded grap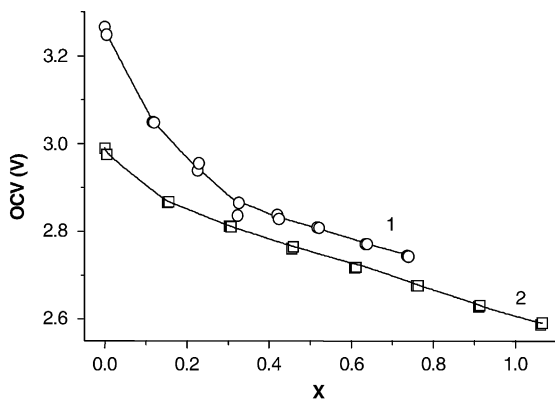hite or acetylene soot as a electroconducting additives. The differences in OCV corresponding to $x = 1$ are equal to 0.52 and 0.40 V, respectively. These values correlate reasonably well with those predicted theoretically (Table 2) [21]. The value of the OCV changes reported by Kawakita et al. for the oxygen-deficient lithium–vanadium bronze ($Li_{1+x}V_3O_{8-\delta}$) are very close to our data.

As was mentioned above, four entities with the formula LiV_3O_8 are possible (Fig. 1), and in each of them, vanadium atoms are quadrivalent and exist in the singlet ground state. However, these formulae are essentially different: in the first and second entities, a six-membered ring appears and the number of V=O groups changes from one (in **1**) to four (in **3**). Both V–O–V and V=O fragments were actually found in the synthesised bronzes, and the presence of three different V=O bonds of lengths 0.1586, 0.1584 and 0.1583 nm was confirmed by X-ray analysis [2]. These latter bonds in monolithiated bronze can be assigned to V(III)=O (in **1**), and V(III)=O and V(I)=O (in **4**), since **1** and **4** are energetically the most favourable. The above facts undoubtedly imply that the entities we have considered are fragments of real structures.

The IR spectrum of the synthesised bronze ($Li_{1.3}V_3O_8$) exhibits bands at 1010, 994 and 972 cm^{-1}, which can be assigned to the stretching vibrations of the three above types of V=O groups (Fig. 5) Similar results were reported by Dai et al. for bronze synthesised at 300–350 °C [22]. The absorption at 734 cm^{-1} can be related to the V–O–V stretching vibration. In the case of the oxygen-deficient bronze ($Li_{1+x}V_3O_{8-\delta}$) the relevant peak was observed at 750 cm^{-1} [18]. The absorption between 600–400 cm^{-1} most probably arises from V–O–V and V=O bending vibrations, while that at 295, 212, 161 and 86 cm^{-1} can be related to the deformation of the polynuclear chain consisting of Li–O-fragments [13]. Lastly, the absorption in the region 3550–3350 cm^{-1} and that at 1615 cm^{-1} are probably due to Li–O-stretching vibrations.

Theoretical calculations (Table 3) indicate that modes at high wave numbers (the region between 3550 and 3350 cm^{-1}) correspond to Li–O-stretching vibrations. For bronzes with different degrees of lithiation the intensity of bands between 3400–3330 cm^{-1} increases somewhat when the number of intercalated Li atoms increases. This absorption shifts to 2996 cm^{-1} if $x = 0$, When $x = 3$, the band splits into two peaks. An increase in the degree of
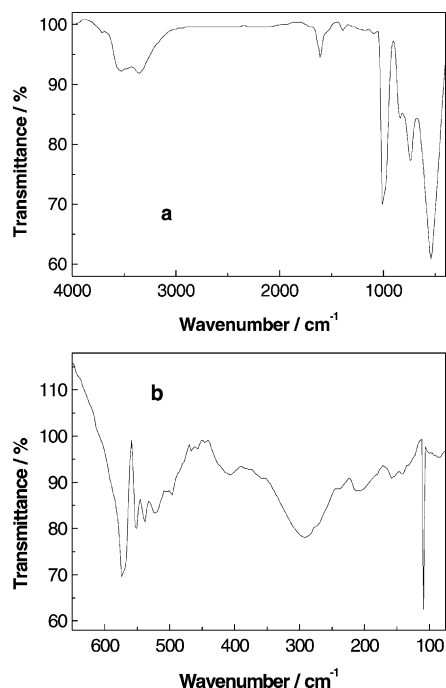

Fig. 4. The OCV changes in the $Li_{1+x}V_3O_8$/1.0 N $LiClO_4$ + propylene carbonate/Li cell vs. the intercalated lithium stoichiometric coefficient (x) for two different electroconducting additives-acetylene soot (1) and expended graphite (2).

Fig. 5. The IR transmission spectra of the initial lithium–vanadium bronze $Li_{1+x}V_3O_8$, $(x \approx 0, 3)$ in the (a) 4000–500 cm^{-1} and (b) 100–650 cm^{-1} ranges.

Table 3
Theoretically predicted wave numbers (in cm^{-1}) of vibrational modes of $Li_xV_3O_8$

$Li_1V_3O_8$ (1)	$Li_2V_3O_8$ (1a)	$Li_3V_3O_8$ (5b)	$Li_4V_3O_8$ (6)
2996 s	3405 w	3331 m	3400 w
1241 s	1522 w	1519 w	3373 m
831 m	1123 m	1153 m	1501 m
781 w	1023 s	709 s	1083 m
624 m	734 s	596 w	1047 s
483 w	610 m	595 s	886 s
345 w	506 s	341 w	873 w
321 w	474 s	302 w	824 m
212 w	422 s	160 w	597 s
	338 m	132 m	481 s
	283 m	114 m	450 m
	261 s	88 m	374 s
	178 s	48 m	302 m
	102 m		234 m
	85 m		212 w
			157 m
			107 m

lithiation enhances low-frequency modes which, as mentioned above, correspond to the deformations of the polynuclear chain.

Therefore, the proposed forms of $Li_{1+x}V_3O_8$ are a good reflection of the actual interatomic bonding in lithium–vanadium bronzes. It should be noted, however, that the real bronzes are infinite structures made up of fragments of the entities we have been considering.

5. Conclusions

The structure and properties of lithium trivanadates were examined with respect to the model molecules constructed following the classical valence theory. Four entities with the formula LiV_3O_8, 14 with $Li_2V_3O_8$, two with $Li_3V_3O_8$ and one with $Li_4V_3O_8$ were selected for theoretical examination. The energetic characteristics of some of these entities were used to estimate OCV changes during the lithiation of $Li_{1+x}V_3O_8$. For the insertion of the first lithium atom, the calculated value of the OCV change is 0.559 V, while the experimental values are 0.52 and 0.40 V for electrodes filled with expanded graphite and acetylene soot, respectively. The correlation between the calculated and experimental values of the OCV changes for the lithiation process was also good when the second and third lithium atoms were inserted [10]. The results obtained for the model molecules, form a convenient basis for modelling the bronze clusters (containing 64 and 128 atoms). This is one of the issue on which we are currently focusing our attention.

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