



New ramsdellites $\text{LiTi}_{2-y}\text{V}_y\text{O}_4$ ($0 \leq y \leq 1$): Synthesis, structure, magnetic properties and electrochemical performances as electrode materials for lithium batteries

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ABSTRACT

The new ramsdellite series $\text{LiTi}_{2-y}\text{V}_y\text{O}_4$ ($0 \leq y \leq 1$) has been prepared by conventional solid state chemistry techniques and was characterized by X-ray powder diffraction and electron diffraction. To our knowledge, this is the first report on ramsdellites containing vanadium. The magnetic behaviour of these ramsdellites is strongly influenced by its vanadium content. In this sense, LiTi_2O_4 ($y=0$) exhibits metallic-like temperature independent paramagnetism, but d electrons tend to localize with increasing V content. LiTiVO_4 , though also paramagnetic, follows then the Curie–Weiss law. The crossover from delocalized to localized electrons is observed between compositions $y=0.6$ and 0.8 . For $y \geq 0.8$ the magnetic results evidence an isovalent substitution mechanism of trivalent Ti by V. The electrochemical lithium intercalation and deintercalation chemistry of $\text{LiTi}_{2-y}\text{V}_y\text{O}_4$ is grouped into two different operating voltage regions. Reversible lithium deintercalation of vanadium-substituted ramsdellite titanates $\text{LiTi}_{2-y}\text{V}_y\text{O}_4$ in the high voltage range 2–3 V vs. Li occurs in two main steps, one at about 2 V and the other at about 3 V. The 3 V process capacity increases with the vanadium content, while the 2 V capacity decreases at the same time. The vanadium to titanium substitution rate in LiTi_2O_4 was found to be beneficial to the specific energy in as much as a 50% increase (1 V) of the working voltage is observed. On the other hand, reversible lithium intercalation in vanadium-substituted ramsdellite titanates $\text{LiTi}_{2-y}\text{V}_y\text{O}_4$ in the low voltage range 1–2 V vs. Li occurs in one main single step, in which the capacity is not affected by the vanadium content, although vanadium-doping produces an improved capacity retention with an excellent cycling behaviour observed for $y \leq 0.6$.

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1. Introduction

Lithium titanates belong to the most widely considered metal oxides for low potential applications and are thought to be promising future alternatives to the presently used anode materials. An insertion reaction governs the electrochemical process in these oxides, going with the partial or complete reduction of Ti^{4+} to Ti^{3+} at relative low voltage (1.5–1 V vs. Li). Usually a single-phase process accompanied by smooth and reversible voltage vs. composition dependence is preferred to a two-phase process. This is because the latter usually involves structural (volume) changes known to be highly detrimental to capacity retention upon cycling. However, a two-phase domain does not necessarily imply a large volume change. For instance, the spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is a well-known zero-strain insertion material, in spite of the two-phase redox process involved, due to the almost negligible changes in the unit cell on Li insertion [1,2].

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Other promising candidates to anode applications are ramsdellite titanates. $\text{Li}_2\text{Ti}_3\text{O}_7$ is the best-known ramsdellite that reversibly intercalates a large amount of lithium accompanied by a low internal stress [3,4] which is at the origin of its good cycling behaviour. More recently, TiO_2 with ramsdellite structure, which is readily obtained by both chemical or electrochemical oxidation of the high temperature ramsdellite form of LiTi_2O_4 [5] has been proposed as negative electrode [6,7].

Ramsdellite LiTi_2O_4 itself exhibits excellent electrochemical properties in both reduction and oxidation, i.e. it can either intercalate more lithium (to form $\text{Li}_{1+x}\text{Ti}_2\text{O}_4$) or lithium can be extracted from it (leading to $\text{Li}_{1-x}\text{Ti}_2\text{O}_4$) [6,7], leading to a maximum theoretical capacity of 335 mAh g^{-1} . In practise only the former process would be useful for negative electrode use in rechargeable lithium ion batteries [7], that is the low voltage capacity (1.5–1 V vs. Li, see also Fig. 1). This explains why the maximum useful capacity as negative electrode of both ramsdellites, $\text{Li}_2\text{Ti}_3\text{O}_7$ and LiTi_2O_4 , are finally very similar (175 mAh g^{-1}). In a recent *in situ* study by means of synchrotron radiation [8] we proved that the two-phase redox process involved during Li insertion into LiTi_2O_4 (leading to $\text{Li}_2\text{Ti}_2\text{O}_4$) is accompanied by very slight volume changes. This zero-strain

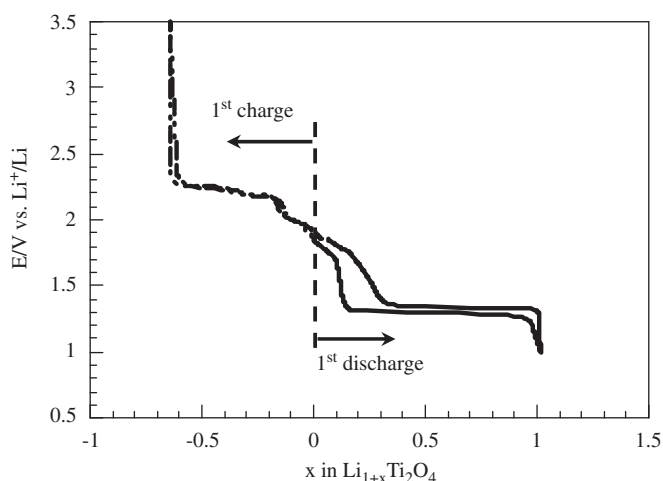


Fig. 1. Voltage composition curve for LiTi_2O_4 showing the first reduction (intercalation-deintercalation) cycle (solid line) and the first oxidation (deintercalation-intercalation) cycle (dotted line). (Adapted from ref.⁹).

behaviour then accounts for the excellent capacity retention upon cycling. Regarding lithium extraction from LiTi_2O_4 , a continuous variation of voltage between 2 and 3 V vs. Li^+/Li is observed (Fig. 1).

To summarize, the electrochemical behaviour of LiTi_2O_4 ($\text{LiTi}^{4+}\text{Ti}^{3+}\text{O}_4$) is characterised by the $\text{Ti}^{4+} \rightarrow \text{Ti}^{3+}$ reduction at low 1.5–1 V and the $\text{Ti}^{3+} \rightarrow \text{Ti}^{4+}$ oxidation at higher 2–2.5 V. Substitutions of Ti^{3+} by other trivalent metals have been tried in LiTi_2O_4 in order to improve the electrochemical properties. Vanadium and chromium substitution, e.g. LiTiVO_4 and LiTiCrO_4 lead to successful results with an increase of the operating voltage during oxidation beyond 3 V [9,10]. These new ramsdellites are then interesting as new high voltage electrode materials. The present work is dealing with the preparation of a complete solid solution of new vanadium-substituted ramsdellites $\text{LiTi}_{2-y}\text{V}_y\text{O}_4$ ($0 \leq y \leq 1$) and its structural and magnetic characterization. This paper reports results that allow evaluating the electrochemical behaviour of these materials, e.g. the effect that has the vanadium substitution on both the low voltage (1.5–1 V) intercalation process and the high voltage (2–2.5 V) lithium de-intercalation process.

2. Experimental section

Crystalline $\text{LiTi}_{2-y}\text{V}_y\text{O}_4$ with the following nominal compositions: $y=0.2, 0.4, 0.6, 0.8$ and 1.0 was prepared by conventional solid-state reaction. Mixtures containing appropriate amounts of high purity TiO_2 (anatase), Ti_2O_3 and V_2O_3 and Li_2TiO_3 were wrapped with copper foil to avoid reaction with the container walls, charged into quartz ampoules and sealed under dynamic vacuum. Li_2TiO_3 itself was previously prepared by reaction of Li_2CO_3 and TiO_2 at 700 °C. Reaction mixtures were heated for two days to temperatures ranging from 950 to 1050 °C, depending on y . Products were finely quenched to room temperature and characterized by powder XRD. Unit cell parameters and integrated intensities were extracted from the pattern using FULLPROF [11] and structure refinement was done by means of Rietveld analysis [12]. In addition, crystal symmetry was checked by means of electron diffraction on a JEOL 2000 electron microscope instrument.

Chemical analysis of titanium and vanadium was performed by means of X-ray energy-dispersive spectroscopy (X-EDS) on a FEG200 Philips electron microscope instrument. Chemical Ti:V ratios were determined in a large number of thin crystallites

exhibiting ramsdellite-characteristic electron diffraction patterns, in order to guarantee reliability of the microanalysis.

Magnetic measurements were performed in a conventional SQUID magnetometer. Samples were cooled down to 4 K in zero magnetic field (ZFC). Magnetic susceptibility was measured while heating samples in a magnetic field of 50 Oe. Previous to calculations the corrections of the diamagnetic contribution from the ion cores have been made [13,14].

The electrochemical performance of $\text{LiTi}_{2-y}\text{V}_y\text{O}_4$ was tested in nonaqueous solution using SwagelokTM test cells. Cells were assembled in an argon-filled glove box and used 1 M LiPF_6 in 2:1 (v/v) EC/DMC as electrolyte, whose high stability against oxidation is well known [15], and glass fibre as separator (EC=ethylene carbonate, DMC=dimethyl carbonate). The positive electrode was prepared by pressing a powdered mixture of $\text{LiTi}_{2-y}\text{V}_y\text{O}_4$, carbon black and a binder (Kynarflex) in a 85:10:5 weight ratio. Lithium foil served as negative electrode.

Galvanostatic lithium deinsertion/insertion reactions were performed with a MacPile II system from Biologic at a constant current density of 0.1 mA cm^{-2} . Cells were cycled from the rest potential to 1 V and 4.2 V, respectively. Experiments under equilibrium conditions were conducted by the galvanostatic intermittent titration technique (GITT) with a constant current density of $\pm 0.04 \text{ mA cm}^{-2}$, which was applied during 0.2 h. Current was then switched off and the cell was allowed to relax during 4 h before the next current cycle was started.

3. Results and discussion

3.1. Synthesis and structural characterization

Darkish brown to black powders were obtained after reaction of appropriate amounts of the reactants described in the experimental section at temperatures ranging from 950 to 1050 °C.

X-ray diffraction patterns of all $\text{LiTi}_{2-y}\text{V}_y\text{O}_4$ compositions ($y=0.2, 0.4, 0.6, 0.8$ and 1.0) are similar to that reported for LiTi_2O_4 (i.e. the $y=0$ member) [5,7] and could be indexed in the orthorhombic system (S.G. *Pbnm*). Powder X-ray diffraction studies therefore confirm the existence of the ramsdellite solid solution in the whole compositional range $\text{LiTi}_{2-y}\text{V}_y\text{O}_4$ ($0 \leq y \leq 1$).

Unit cell parameters were in good accord with the values expected from the proposed solid solution mechanism (Table 1), $\text{LiTi}_{2-y}\text{V}_y\text{O}_4$, which comprises an isoivalent substitution of Ti^{III} by V^{III} . Both a and b become slightly smaller (0.4% and 0.7%, respectively) with vanadium content, while c remains practically unchanged when going from LiTi_2O_4 to LiTiVO_4 . The observed slight contraction is in agreement with the Shannon's ionic radii [16], for which the average octahedral ionic radii of the central ions are 0.64 Å (50% Ti^{3+} and 50% Ti^{4+}) and 0.62 Å (50% V^{3+} and 50% Ti^{4+}), respectively (sizes used of the "pure" Ti^{3+} and V^{3+} ions in octahedral coordination were 0.67 and 0.64 Å, respectively).

Table 1

Unit cell parameters from X-ray powder diffraction and reliability factors for members of the ramsdellite solid solution $\text{LiTi}_{2-y}\text{V}_y\text{O}_4$ ($0 \leq y \leq 1$).

y	a (Å)	b (Å)	c (Å)	V (Å)	R_B	χ^2
0	5.0310(1)	9.6264(2)	2.94243(5)	142.503(5)	0.055	1.33
0.2	5.0261(2)	9.6112(3)	2.94368(6)	142.199(6)	0.052	1.21
0.4	5.0176(2)	9.5857(2)	2.94434(6)	141.615(7)	0.052	1.47
0.6	5.0160(2)	9.5802(2)	2.94522(4)	141.601(6)	0.055	1.35
0.8	5.0141(1)	9.5718(2)	2.94966(4)	141.565(4)	0.045	1.31
1.0	5.00900(8)	9.5571(1)	2.94242(3)	140.875(3)	0.049	1.38

Space group is *Pbnm*.

It is noteworthy to mention that a similar observation was made by Hayakawa et al. [13] for the spinel series $\text{LiTi}_{2-y}\text{V}_y\text{O}_4$, which is the low temperature form. For the respective spinel form, cubic cell parameters $a=8.40\text{ \AA}$ in LiTi_2O_4 and 8.35 \AA in LiTiVO_4 have been reported, which represents a volume decrease of 1.8%, when titanium is substituted by vanadium. For the ramsdellite form the observed difference in the unit cell volume is practically the same, 1.2%, when going from lithium titanate to lithium vanadium titanate.

Structural data of LiTi_2O_4 has been used as initial model for the structure refinement of all ramsdellites $\text{LiTi}_{2-y}\text{V}_y\text{O}_4$. It was supposed that the Ti position is randomly occupied by Ti and V in their respective nominal composition as electron diffraction experiments suggested (see below). Fig. 2 shows, as an example, the corresponding Rietveld refinement plot with the fitting results of the X-ray data belonging to LiTiVO_4 ($y=1$).

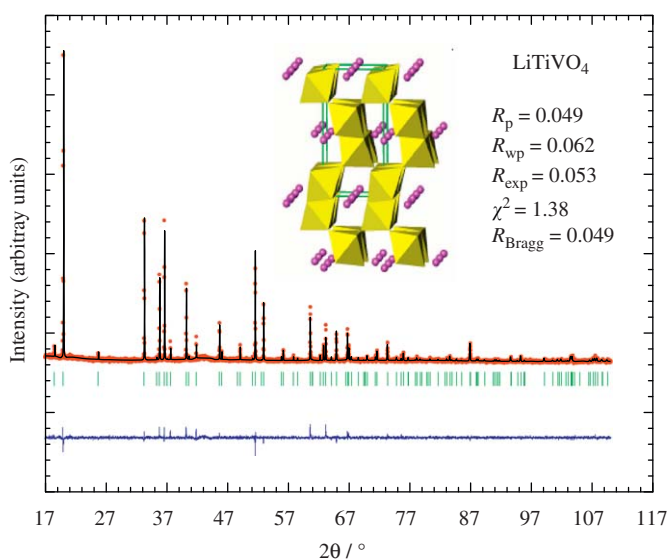


Fig. 2. Graphical result of the Rietveld refinement of LiTiVO_4 . The inset shows the arrangement of $[\text{TiO}_6]$ octahedra and Li atoms (spheres) in the ramsdellite structure.

As vanadium and titanium are not distinguishable by X-rays due to its very close number of electrons, X-EDS microanalysis has been used to check the chemical composition regarding both metals. Average percentages regarding Ti and V obtained for $\text{LiTi}_{2-y}\text{V}_y\text{O}_4$ were homogenous for each composition and remarkably close to the nominal metals ratios. Indeed, for $y=1$ the calculated Ti/V ratio is 1.0. Therefore, we will refer hereafter to all samples by their nominal compositions. Selected area diffraction (SAED) patterns of all $\text{LiTi}_{2-y}\text{V}_y\text{O}_4$ samples showed always the lattice spots of a primitive orthorhombic cell with $a \approx 5.0\text{ \AA}$, $b \approx 9.6\text{ \AA}$, $c \approx 2.9\text{ \AA}$, consistent with the ramsdellite lattice. As an example, five selected zone axis are illustrated for LiTiVO_4 ($y=1$) in Fig. 3.

The lack of extra reflections let us conclude that both heavy metals are randomly distributed over the octahedral sites. Indeed, ordering of Ti and V over the octahedral sites was not expected to occur, as the ionic radii are quite similar (V^{3+} : 0.64 \AA ; Ti^{4+} : 0.605 \AA , both at octahedral sites) [16].

3.2. Magnetic characterization: the oxidation state of Ti and V

The variation of the magnetic susceptibility with temperature in the ramsdellites series $\text{LiTi}_{2-y}\text{V}_y\text{O}_4$ has been analysed in order to get information about the oxidation states of Ti and V.

The magnetic behaviour of LiTi_2O_4 , this is the $y=0$ member of the series, has been previously reported for single crystals [17]. It exhibits a nearly temperature independent paramagnetism (TIP) in the range of $100\text{--}300\text{ K}$ (see Fig. 4), that has been interpreted as due to the metallic character of the oxide. Below 100 K , a sharp upturn in magnetic susceptibility was observed, which has been attributed to localized electron paramagnetic states or paramagnetic impurities [17]. Therefore, in the high temperature range an intermediate oxidation state rather than localized Ti^{4+} and Ti^{3+} ions for every titanium atom gives a better picture for this oxide.

The magnetic behaviour of ramsdellite LiTi_2O_4 is then different from that reported for other oxides of same chemical composition: spinel LiTi_2O_4 becomes superconducting below 12 K [18] and chemically lithiated anatase $\text{Li}_{0.5}\text{TiO}_2$ follows a Curie–Weiss-like behaviour in the temperature range $10\text{--}200\text{ K}$ [19]. Similar magnetic behaviours to that reported for ramsdellite LiTi_2O_4 are

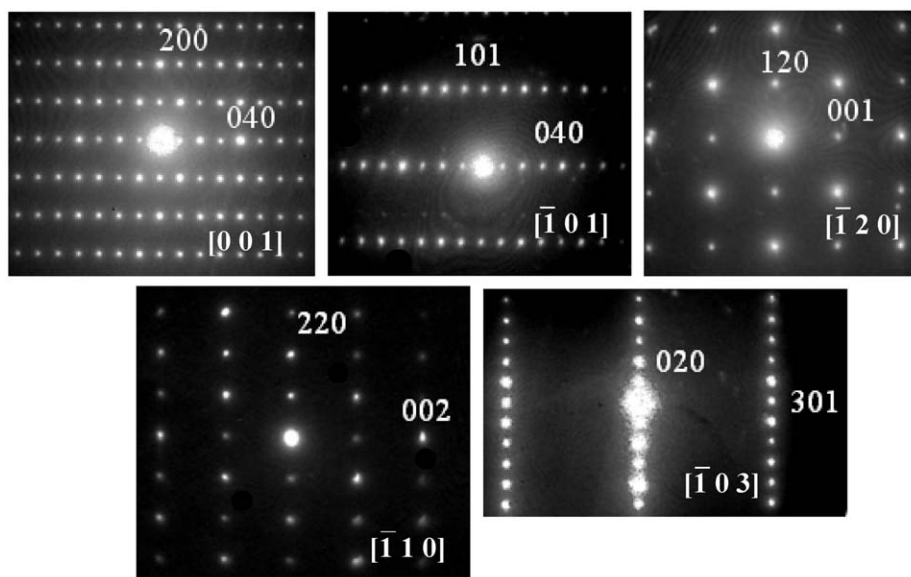


Fig. 3. SAED patterns of $\text{LiTi}_{2-y}\text{V}_y\text{O}_4$ compounds obtained along different zone axis.

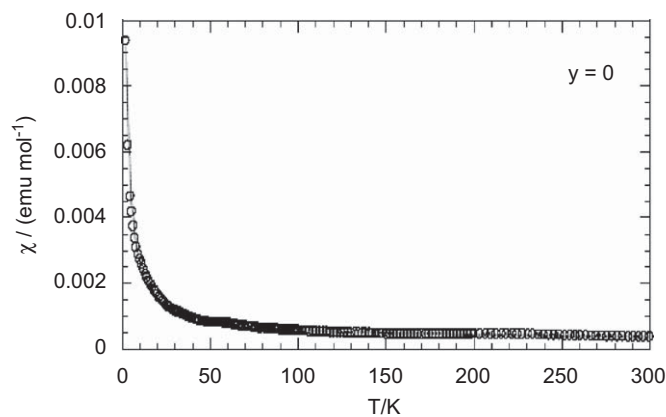


Fig. 4. The magnetic susceptibility of LiTi_2O_4 in the temperature region 2–300 K.

found in ramsdellites $\text{LiTi}_{2-y}\text{V}_y\text{O}_4$ with compositions $y=0.2, 0.4$ and 0.6 . In these the magnetic susceptibilities are almost temperature-independent above 50 K, as can be seen in Fig. 5a, where the variation of the inverse molar magnetic susceptibility (χ_m^{-1}) is represented vs. temperature. Based on this result, an intermediate oxidation state rather than localized ions for every metal should then be viewed as the more likely in the high temperature range, as already seen for LiTi_2O_4 .

However, an important difference is that the magnetic susceptibility (primarily the temperature-independent part of total susceptibility) steadily increases with vanadium content. This result could be explained by the increasing number of electrons that are released to the conduction band on doping the samples with vanadium, when we take into consideration that a d^1 cation (Ti^{3+}) is being replaced by a d^2 cation (V^{3+}). Similar to ramsdellite LiTi_2O_4 , a sharp upturn in magnetic susceptibility was observed below 100 K, which can principally be attributed to (a) localized electron paramagnetic states or (b) paramagnetic impurities [17].

Regarding the former possibility, the susceptibilities can then be expressed with an equation, which comprises a temperature independent part χ_0 and a Curie–Weiss term. χ – T curves were best fitted when an additional temperature dependent term $A_{\text{TD}} \cdot T$ was included, similar to the results reported for spinel LiTi_2O_4 above the superconducting transition temperature [20]:

$$\chi = \chi_0 + \frac{C}{T - \theta} + A_{\text{TD}} \cdot T \quad (1)$$

Fitting the magnetic susceptibilities data in the whole temperature range according to Eq. (1) yielded effective magnetic moments of 1.0, 1.37 and $1.81\mu_B$ for $\text{LiTi}_{1.8}\text{V}_{0.2}\text{O}_4$, $\text{LiTi}_{1.6}\text{V}_{0.4}\text{O}_4$ and $\text{LiTi}_{1.4}\text{V}_{0.6}\text{O}_4$, respectively. These values are clearly lower than those expected for completely localized metal ions states.

On the other hand, the magnetic susceptibility of samples with high vanadium content, i.e. $y=0.8$ and 1.0 is temperature dependent in the whole analysed temperature range (see Fig. 5b). The variation of $1/\chi_m$ in Fig. 5b follows a linear dependence with temperature as expected for a Curie–Weiss paramagnetic material. At low temperature the curve deviates from linearity likely due to antiferromagnetic interactions. Fitting of data in the high temperature region (200–300 K) according to the Curie–Weiss law yielded effective magnetic moments of $2.67\mu_B$ and $2.73\mu_B$ for $\text{LiTi}_{1.2}\text{V}_{0.8}\text{O}_4$ and LiTiVO_4 , respectively. These values are in agreement with the expected values for replacement of Ti^{3+} by V^{3+} ($2.65\mu_B$ and $2.83\mu_B$, respectively).

To sum up the results obtained from magnetic measurements, it can be said that a transition from delocalized to localized

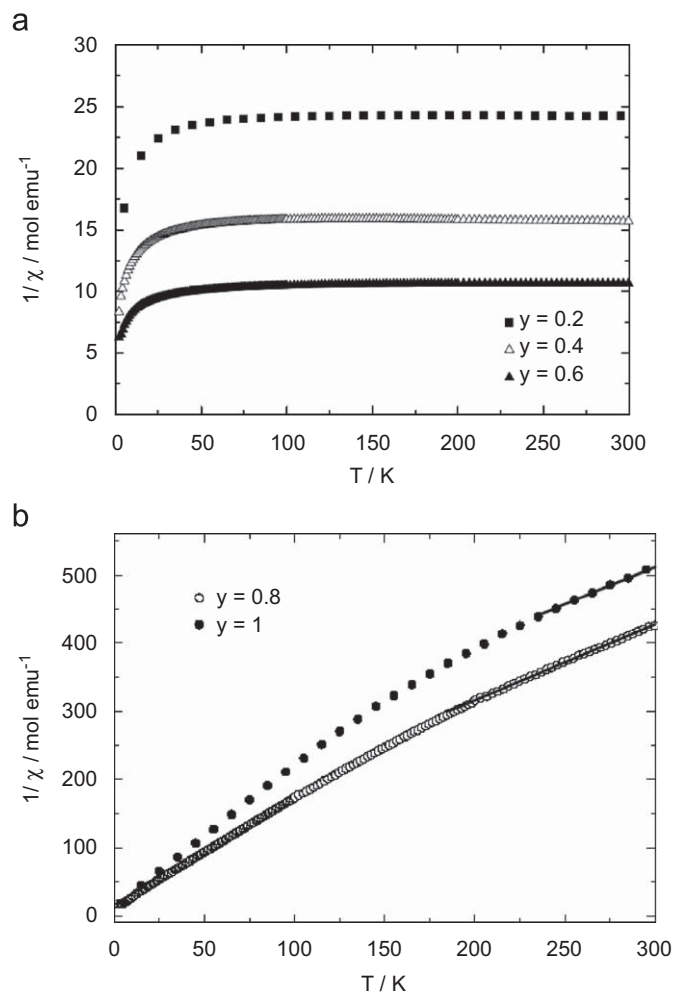


Fig. 5. (a) The inverse susceptibility for $\text{LiTi}_{2-y}\text{V}_y\text{O}_4$ ($y=0.2, 0.4$ and 0.6) as functions of temperature. (b) Inverse molar susceptibility of $\text{LiTi}_{1.2}\text{V}_{0.8}\text{O}_4$ ($y=0.8$; open circles) and LiTiVO_4 ($y=1.0$; filled circles).

electrons occurs when vanadium content increases along the substitution of Ti^{3+} by V^{3+} . Complementary measurements of electrical resistivity and Seebeck coefficients would be required for a more detailed characterization of the transition from delocalized to localized electrons in $\text{LiTi}_{2-y}\text{V}_y\text{O}_4$ ramsdellite materials. Hayakawa et al. performed such a parallel study in the analysis of the metal–insulator transition occurring in the $\text{LiTi}_{2-y}\text{V}_y\text{O}_4$ spinel system [13].

3.3. Electrochemical characterization

3.3.1. Li intercalation into $\text{LiTi}_{2-y}\text{V}_y\text{O}_4$

The first discharge curves of the ramsdellite series $\text{LiTi}_{2-y}\text{V}_y\text{O}_4$ for $0 \leq y \leq 1$ obtained at a constant current density of 0.1 mA cm^{-2} starting from the rest potential of the cell down to 1 V are illustrated in Fig. 6. All compositions present a very similar behaviour: the operating voltage first decreases continuously starting from its rest (open-circuit) potential (labelled as I in Fig. 6). It is well known that a continuously changing potential with degree of insertion reflects the formation of a solid solution, since a continuous variation of composition occurs along the insertion reaction. This solid solution region is then followed by a constant voltage behaviour (plateau) located at circa 1.4 V (labelled as II in Fig. 6). This invariant potential is characteristic for the equilibrium of two phases with differing degrees of Li

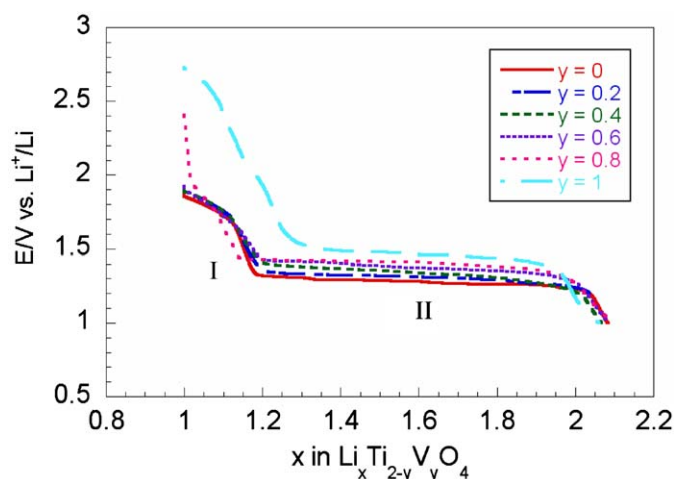
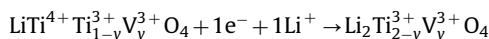


Fig. 6. Typical voltage composition curve for the first discharge of Li/LiTi_{2-y}V_yO₄ cells with 0 ≤ y ≤ 1. The current density was 0.1 mA cm⁻².

insertion. A synchrotron diffraction study performed on ramsdellite LiTi₂O₄ recently proved that a solid solution region is followed by a two-phase regions when going from LiTi₂O₄ to Li₂Ti₂O₄ [8] with the concomitant reduction of all Ti⁴⁺ to Ti³⁺. The vanadium substituted LiTi_{2-y}V_yO₄ of this work exhibit the same electrochemical intercalation characteristic. The fact that both the shape of the voltage profile and the total amount of intercalated lithium are the same for the complete series LiTi_{2-y}V_yO₄ point to the presence of those same processes for every composition. Even the limit of insertion at the end of discharge corresponded to 1 Li per formula, independently from the vanadium content. Therefore the following one-electron count is proposed for the complete series during the Li intercalation down to 1 V:



Due to the very similar atomic weights of Ti and V, the capacity values of LiTi_{2-y}V_yO₄ materials remains practically invariant and close to 160 mAh g⁻¹. Furthermore, we have observed that capacity loss is drastically reduced by the substitution of Ti by V. Initial discharge capacities for ramsdellites ranged from 161 mAh g⁻¹ (y=0; LiTi₂O₄) to 155 mAh g⁻¹ (y=1; LiTiVO₄). For LiTi₂O₄ (y=0) capacity values rapidly decrease from 161 to 100 mAh g⁻¹ by cycle three (38% capacity loss), although being from hereon stable for the next 50 cycles. Similar results have been reported for LiTi₂O₄ by other authors [6]. For the material with highest vanadium content, LiTiVO₄ (y=1), the initial discharge capacity is practically maintained upon cycling. Partly substituting titanium by vanadium is then beneficial to the electrochemical performance (capacity, cyclability) of the ramsdellite material.

It is observed that the average intercalation voltage of LiTi_{2-y}V_yO₄ materials increased with increasing V content (Fig. 6). In order to find out whether the observed variation of cell voltage was due to extrinsic (e.g. cell polarization) or really related to intrinsic properties of each material, cells were discharged under quasi-equilibrium conditions using identical experimental conditions (current density, temperature) for each material. Then, the reduction potential was measured for each composition at a given intercalation rate of x=0.5 in Li_{1+x}Ti_{2-y}V_yO₄ at the centre of the discharge plateau. The result of measuring the voltages under these conditions (fixed Li intercalation degree, under equilibrium) was that the reduction potential increased progressively from 1.327 V (y=0) to 1.504 V (y=1). This is a clear indication that the observed variation of cell voltage is directly related to substitution. The vanadium content enables then fine monitoring of the average intercalation voltage (see also Fig. 7).

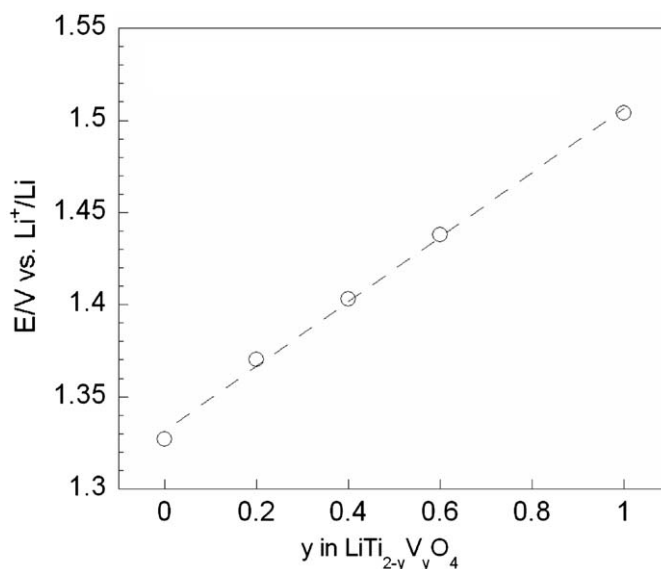


Fig. 7. Discharge voltage of Li_{1+x}Ti_{2-y}V_yO₄ under equilibrium conditions measured at a lithium intercalation rate x=0.5 as function of the vanadium content.

The change of cell working voltage is thought to be due to a change of the Fermi energy of the oxide, resulting in a change of the reduction potential vs. Li⁺/Li. The change of Fermi energy must then be connected to the partial substitution of Ti³⁺ by V³⁺. A possible explanation could be that V has more internal *d* orbitals than Ti has. As a consequence, the energy of the Fermi level will be expected to decrease progressively with increasing V content, and at the same time the reduction potential vs. Li⁺/Li will raise. In any case, calculations of band structure and the working voltage of LiTi_{2-y}V_yO₄ materials having different V amount would be useful to confirm this point.

3.3.2. Li extraction from LiTi_{2-y}V_yO₄

The charge curves of the materials reported in Fig. 8a were obtained when cells were charged up to 4.2 V. For 0 ≤ y ≤ 1, lithium intercalation occurs in two main steps, one at about 2.3 V and the other at about 3.1 V. The first (2.3 V) is the only process occurring during lithium deinsertion from LiTi₂O₄ (the y=0 member of the present series), being associated to the Ti^{4+/3+} redox couple. A detailed study of the lithium deintercalation reaction in LiTi₂O₄ ramsdellite using synchrotron radiation showed recently that this process truly consists of a solid solution regime centred at 2.1 V for lower degrees of lithium extraction, followed by a main two-phase equilibrium at 2.3 V. The complete conversion to the lithium-free ramsdellite Ti₂O₄ (or TiO₂) is accomplished at the end of the charge process [8].

The capacity of the 2.1–2.3 V process of the present LiTi_{2-y}V_yO₄ materials decreases with increasing vanadium content, or what is the same, as titanium content decreases. When materials with y > 0 were charged at higher voltage, a new deintercalation process is observed at about 3.1 V, whose capacity increases with increasing vanadium content. This new process is then related to the presence of V³⁺. Note that LiTiVO₄ shows a single high voltage process at 3.1 V without any capacity at the lower 2.3 V, since for y=1 Ti³⁺ is supposed to be completely substituted by V³⁺. These observations are in agreement with a simple isoivalent substitution mechanism of Ti³⁺ by V³⁺ for the series LiTi_{2-y}V_yO₄. The existence of such a simple substitution mechanism of the trivalent ion, e.g. Ti³⁺ by V³⁺, in LiTi_{2-y}V_yO₄ ramsdellites is further supported by the results obtained from

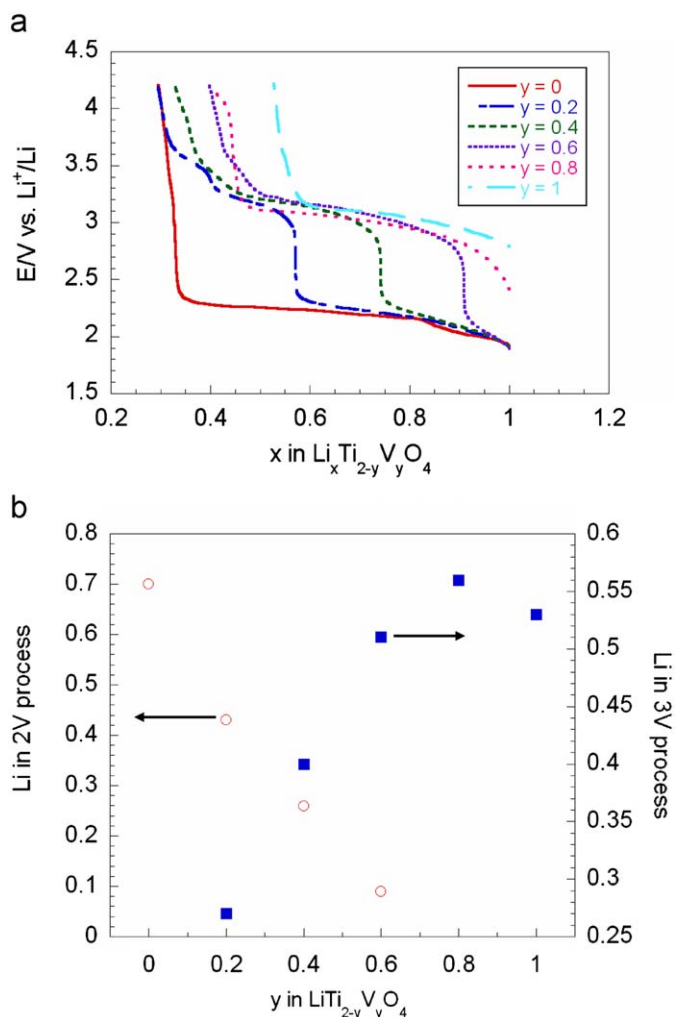


Fig. 8. (a) First charge to 4.2 V of $\text{LiTi}_{2-y}\text{V}_y\text{O}_4$ materials for $0 \leq y \leq 1$ at a current density 0.1 mA cm^{-2} . (b) Variation of the lithium quantity involved in the ca. 2 V and ca. 3 V processes with vanadium content in $\text{LiTi}_{2-y}\text{V}_y\text{O}_4$.

magnetic measurements (see paragraph 3.2.). In these, agreement of experimental and calculated magnetic moments in the compositions showing a Curie–Weiss behaviour verified the replacement of Ti^{3+} by V^{3+} .

Only for the composition $\text{LiTi}_{1.8}\text{V}_{0.2}\text{O}_4$ ($y=0.2$), the high voltage process centred at ca. 3.2 V, develops an additional capacity at slightly higher 3.5 V. This electrochemical detail is observable in both Fig. 8a (dotted line corresponding to $y=0.2$) and in Fig. 9b. Then we cannot exclude, for the composition $y=0.2$, the possibility of a further vanadium redox couple, e.g. $\text{V}^{4+/5+}$, which has been reported to operate at higher 3.5 V during the lithium insertion into V_2O_5 . The origin of such extra capacity could then be likely due to the presence of a small fraction of additional V^{4+} ions in the composition $y=0.2$.

The amount of lithium involved in the ca. 2 and ca. 3 V deinsertion process are generally smaller than those calculated taking into account the respective nominal compositions. The deinsertion process is then likely to be kinetically slower than those observed during insertion. A better agreement of experimental capacities delivered in the 2 and 3 V processes with calculated values is achieved when cells are charged under equilibrium conditions. However, the necessary long-time charges at high voltages favours side reactions due to electrolyte oxidation. From the data reported in Fig. 8a it can be shown that the vanadium content of the ramsdellites enables monitoring of

the quantity of Li involved in both 2.3 and 3.1 V processes. The former is seen to decrease linearly with vanadium content, whereas the latter does the opposite, as depicted in Fig. 8b.

The total specific capacity in the high voltage range (between 2 and 3 V ca. 160 mAh g^{-1} for an electron count) of materials remains almost invariant independent of the vanadium content. However, a great benefit is obtained from substituting titanium by vanadium, as the de-insertion process is raised by 1 V, from ca. 2 to 3 V. The 3 V process occurring in the vanadium containing materials is high enough to consider $\text{LiTi}_{2-y}\text{V}_y\text{O}_4$ as interesting materials for the positive electrode in lithium batteries, as recently proposed [9].

A partial substitution of titanium by vanadium is then beneficial to the total specific energy of the ramsdellite material, leading to a maximum specific energy of 510 mWh g^{-1} , 50% higher than that of LiTi_2O_4 (340 mWh g^{-1}). Specific theoretical capacity values and operating voltage of the ramsdellite materials with higher vanadium content are even comparable to those reported for LiFePO_4 (170 Ah g^{-1} at average 3.5 V), which is presently one of the preferred cathode materials for lithium batteries [21–26]. On one hand, a high specific energy is an indispensable requirement for a good positive electrode material of a lithium battery. On the other hand, the materials should be able to sustain a large number of charge–discharge cycles with a minimum capacity loss.

Fig. 9 shows the cycling behaviour of various $\text{LiTi}_{2-y}\text{V}_y\text{O}_4$ materials over several cycles. Two main characteristics are observed in relationship to the vanadium content: higher capacity values and low polarization accompanied by good cyclability for materials with low vanadium content, $y \leq 0.6$, and lower capacity values and higher polarization linked to a poorer cyclability for those with higher vanadium content, $y > 0.6$.

The poorer cyclability of the latter is likely to be related to kinetics effects due to the less conducting nature of materials with high vanadium content (an explanation was given in the magnetic characterization section). Cyclability is poorest for $y=1$, whereas a lower capacity loss is observed for $y \leq 0.6$. Slow kinetics is a usual concern in ceramic electrodes with low electronic conductivity (for example LiFePO_4). An optimization of electrode processing (carbon content, particle size, etc.) would be required in order to improve the electrochemical performances of the materials in the high voltage range.

4. Conclusions

A solid solution of vanadium containing ramsdellites $\text{LiTi}_{2-y}\text{V}_y\text{O}_4$ ($0 \leq y \leq 1$) has been synthesized for the first time. These materials are isomorph to LiTi_2O_4 with Ti and V distributed at random over the octahedral positions. Materials with lower V content, $y \leq 0.6$, exhibit an almost temperature independent paramagnetism, while d electrons tend to localize with increasing vanadium content. For $y > 0.6$ a paramagnetic behaviour obeying the Curie–Weiss law is observed. The occurrence of a simple substitution mechanism of Ti^{3+} by V^{3+} is inferred from both magnetic and electrochemical intercalation results.

$\text{LiTi}_{2-y}\text{V}_y\text{O}_4$ materials undergo reversible lithium intercalation when discharged from the rest potential down to 1 V with an average operating voltage of ca. 1.4 V, assigned to the reduction of Ti^{4+} . Discharge capacities for all compositions are close to 160 mAh g^{-1} . The capacity loss upon cycling is drastically reduced with increasing vanadium content.

When charged from the rest potential to 4.2 V, lithium extraction from $\text{LiTi}_{2-y}\text{V}_y\text{O}_4$ occurs in two main steps with operating voltages of ca. 2.3 and 3.1 V, which correspond to the oxidation of Ti^{3+} and V^{3+} , respectively. The capacity of the 2.3 V process decreases for the benefit of the 3.1 V process with

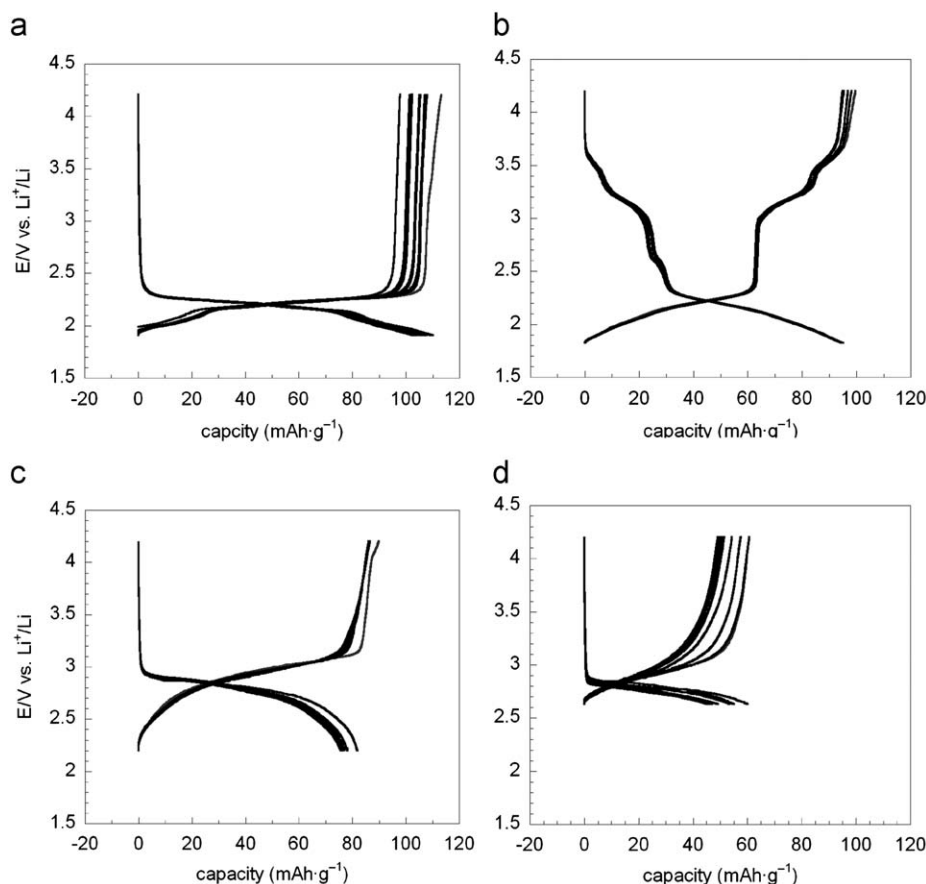


Fig. 9. Cycling characteristics of Li/LiTi_{2-y}V_yO₄ cells at 0.1 mA cm⁻² in the high voltage range (from rest potential to 4.2 V): (a) $y=0$; (b) $y=0.2$; (c) $y=0.8$ and (d) $y=1$.

increasing vanadium content. The increase of voltage due to the substitution of titanium by vanadium in LiTi₂O₄ is then beneficial for the performances of these materials as the positive electrode in lithium batteries, leading to a substantial improvement of the specific energy (50% larger than that of LiTi₂O₄). By contrast, materials with higher vanadium content suffer from a higher capacity loss, which is lower for $y \leq 0.6$. Electrode processing is still needed to overcome the apparent slow kinetics of the high voltage processes, observed in materials with higher vanadium content.

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References

- [1] T. Ohzuku, A. Ueda, N. Yamamoto, *J. Electrochem. Soc.* 142 (1995) 1431–1435.
- [2] S. Scharner, W. Weppner, P. Schmid-Beurmann, *J. Electrochem. Soc.* 146 (1999) 857–861.
- [3] M.E. de Dompablo, E. Moran, A. Varez, F. Garcia-Alvarado, *Mater. Res. Bull.* 32 (1997) 993–1001.
- [4] M.E. de Dompablo, A. Varez, F. Garcia-Alvarado, *J. Solid State Chem.* 153 (2000) 132–139.
- [5] R.K.B. Gover, J.T.S. Irvine, A.A. Finch, *J. Solid State Chem.* 132 (1997) 382–388.
- [6] R.K.B. Gover, J.R. Tolchard, H. Tukamoto, T. Murai, J.T.S. Irvine, *J. Electrochem. Soc.* 146 (1999) 4348–4353.
- [7] A. Kuhn, R. Amandi, F. Garcia-Alvarado, *J. Power Sources* 92 (2001) 221–227.
- [8] A. Kuhn, C. Baethz, F. Garcia-Alvarado, *J. Power Sources* 174 (2007) 421–427.
- [9] A. Kuhn, P. Diaz-Carrasco, M.E. de Dompablo, F. Garcia-Alvarado, *Eur. J. Inorg. Chem.* (2007) 3375–3384.
- [10] A. Kuhn, M. Martin, F. Garcia-Alvarado, *Z. Anorg. Allg. Chem.* 634 (2008) 880–886.
- [11] J. Rodriguez-Carvajal, *Physica B* 192 (1993) 55–69.
- [12] H.M. Rietveld, *J. Appl. Cryst.* 2 (1969) 65.
- [13] T. Hayakawa, D. Shimada, N. Tsuda, *J. Phys. Soc. Jpn.* 58 (1989) 2867–2876.
- [14] K.-H. Hellwege, O. Madelung, in: *Magnetic Properties of Coordination and Organometallic Transition Metal Compounds*, Landolt-Börnstein New Series, vol. 8, Springer, Berlin, 1976.
- [15] C. Sigala, D. Guyomard, A. Verbaere, Y. Piffard, M. Tournoux, *Solid State Ionics* 81 (1995) 167–170.
- [16] R.D. Shannon, *Acta Crystallogr. A* 32 (1976) 751–767.
- [17] J. Akimoto, Y. Gotoh, M. Sohma, K. Kawaguchi, Y. Oosawa, H. Takei, *J. Solid State Chem.* 110 (1994) 150–155.
- [18] D.C. Johnston, H. Prakash, Wh. Zachariassen, R. Viswanathan, *Mater. Res. Bull.* 8 (1973) 777–784.
- [19] D.W. Murphy, M. Greenblatt, S.M. Zahurak, R.J. Cava, J.V. Waszczak, G.W. Hull, R.S. Hutton, *Rev. Chim. Minér.* 19 (1982) 441–449.
- [20] D.C. Johnston, *J. Low Temp. Phys.* 25 (1976) 145–175.
- [21] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, *J. Electrochem. Soc.* 144 (1997) 1188–1194.
- [22] J.M. Tarascon, M. Armand, *Nature* 414 (2001) 359–367.
- [23] B. Kang, G. Ceder, *Nature* 458 (2009) 190–193.
- [24] N. Inamasu, M. Kawamoto, T. Nukuta, T. Tabuchi, Y. Yasunaga, JP2009032678-A.
- [25] C. Okuda, Y. Makimura, I. Sasaki, Y. Takeuchi, Y. Ukyo, S. Kawauchi, M. Mizutani, JP2009004357-A.
- [26] C. Wurm, M. Morcrette, S. Gwizdala, C. Masquelier, WO200299913-A; EP1261050-A; EP1261050-A1; WO200299913-A1; EP1396038-A1; KR2004007591-A; AU2002325218-A1; US2004175614-A1; JP2004529059-W; CN1511352-A; TW589758-A; CN100340018-C; US7371482-B2.