

# Lithium-Rich Rock-Salt-Type Vanadate as Energy Storage Cathode: $\text{Li}_{2-x}\text{VO}_3$

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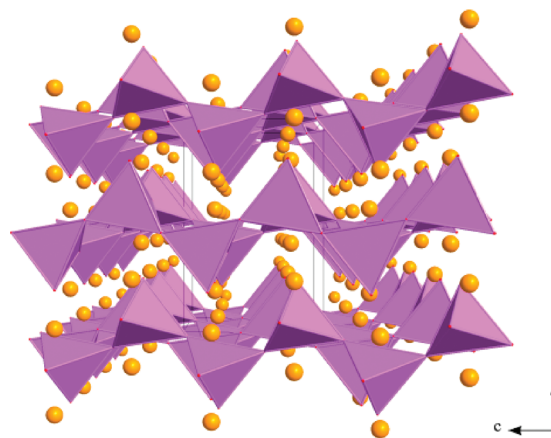
Lithium intercalation in oxides is a topic of the highest importance in view of the commercial realization of batteries for electric vehicles (EV) and hybrid electric vehicles (HEV) as well as microtechnology (Mems, 2D and 3D microbatteries for pacemakers, hearing aids, smart cards, remote sensors, etc.). In this context, the nature of the cathode material has been the object of numerous investigations showing that  $\text{LiCoO}_2$ -based oxides<sup>1</sup> and  $\text{LiFePO}_4$  phosphate<sup>2</sup> are today the best candidates which can be used for this technology. However, the cost and environmental concerns of the cobalt based oxides and the difficulty of optimization and of utilization of  $\text{LiFePO}_4$  necessitate continuous search for new electrode materials that can mitigate these weak points. The renewed interest in the search for new compounds that can be used as potential electrode materials for Li-ion batteries is due to the safety concerns associated with the redox chemistry of the electrode materials. In addition, large scale mobile applications require robust and low cost systems. Several families of materials are screened for this purpose.<sup>1</sup> Intercalation reactions are generally possible in a 3D framework containing interconnected tunnels or on a 2D layered structure. Thus, besides cobalt and iron based oxides, other families of transition metal oxides, involving nickel, manganese, vanadium, titanium, niobium, tungsten, and molybdenum, are of great interest due to their ability to exhibit a mixed valence, with redox potential values in adequation with the batteries applications.

Among the numerous transition metal oxides that have been explored,<sup>3</sup> vanadium oxides appear as attractive electrode materials as they offer the advantages of low cost and abundant sources. This is the case of  $\text{V}_2\text{O}_5$ ,<sup>4</sup> which has been studied for more than 30 years, and of the vanadate  $\text{LiV}_3\text{O}_8$ <sup>5</sup> which received considerable attention as an insertion material. However, the performances of these materials are still unsatisfactory. For instance, attempts to improve the performances of  $\text{V}_2\text{O}_5$  by combining it with more conductive materials such as carbon or nickel show that the resulting composites suffer from low cycling stability.<sup>6</sup> This can be understood by the study carried out by Delmas et al.,<sup>7</sup> which shows that the fully lithiated end member  $\text{Li}_3\text{V}_2\text{O}_5$  of the  $\text{Li}_x\text{V}_2\text{O}_5$  family exhibits the rock salt structure, very different from the layered character of  $\text{V}_2\text{O}_5$ . Moreover, two redox couples,  $\text{V}^{5+}/\text{V}^{4+}$  and  $\text{V}^{4+}/\text{V}^{3+}$ , are involved successively during the lithium intercalation–deintercalation process. As a consequence, the combination of the potential difference between the two redox couples and the structural transition makes the intercalation process difficult to control, leading to its

amorphization on cycling and loss of capacity, so that  $\text{V}_2\text{O}_5$  cannot be used directly as an electrode material.

In contrast, the layered structure of  $\text{LiV}_3\text{O}_8$ <sup>8</sup> built up of  $\text{VO}_6$  octahedra and  $\text{VO}_5$  pyramids, held together by  $\text{Li}^+$  cations, can intercalate two additional  $\text{Li}^+$  cations in its tetrahedral sites, leading to the formula  $\text{Li}_5\text{V}_3\text{O}_8$ .<sup>9</sup> This process involves only one redox couple  $\text{V}^{5+}/\text{V}^{4+}$  and has the advantage of being totally reversible. Nevertheless, this composition, despite much effort to be optimized,<sup>10,11</sup> exhibits a much lower specific capacity of 200 (mA h)/g, compared to  $\text{Li}_3\text{V}_2\text{O}_5$  (290 (mA h)/g). Interestingly, two additional  $\text{Li}^+$  cations can be inserted into this structure, leading to the end member  $\text{Li}_5\text{V}_3\text{O}_8$  with a rock-salt-type structure.<sup>10,11</sup> Unfortunately, its preparation requires a nanoscale synthesis and a partial substitution of vanadium by chromium.

On the basis of the above observations, we have revisited the Li–V–O system. In the latter, the vanadate  $\text{LiVO}_3$  appears as a potential material for lithium insertion due to the unidimensional character of its structure (Figure 1)<sup>12</sup> built up of



**Figure 1.** Structure view of  $\text{LiVO}_3$  along the  $a$  axis.

chains of corner sharing  $\text{VO}_4$  tetrahedra, interconnected through  $\text{LiO}_6$  octahedra. This idea is also supported by the fact that this oxide is a good ionic conductor,<sup>13</sup> suggesting a

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great possibility of structural rearrangements due to the high mobility of lithium cations in such a structure.

Hereby, we demonstrate that the behavior of the tetrahedral structure of  $\text{LiVO}_3$  is quite unusual leading by an irreversible electrochemical reaction to a very different Li-rich compound  $\text{Li}_2\text{VO}_3$  with the rock salt structure. Importantly, we show that this Li-rich rock salt phase is quite stable and can deintercalate up to one lithium cation per formula, with an excellent reversibility at the average potential of 2.5 V vs  $\text{Li}^+/\text{Li}$ . Thus, the Li-rich rock-salt-type phase  $\text{Li}_{2-x}\text{VO}_3$ , with  $0 \leq x \leq 1$ , exhibits a specific capacity of 253 (mA h)/g and a specific energy of 632 (W h)/g, which make it a good candidate as electrode material for Li ion batteries.

$\text{LiVO}_3$  is synthesized by a really simple and conventional solid-state reaction from the stoichiometric amounts of  $\text{Li}_2\text{CO}_3$  and  $\text{V}_2\text{O}_5$ . The initial reagents are first mixed and then heated at 500 °C for 12 h in a platinum crucible under air. The X-ray powder diffraction pattern (Figure 2) of the as-prepared

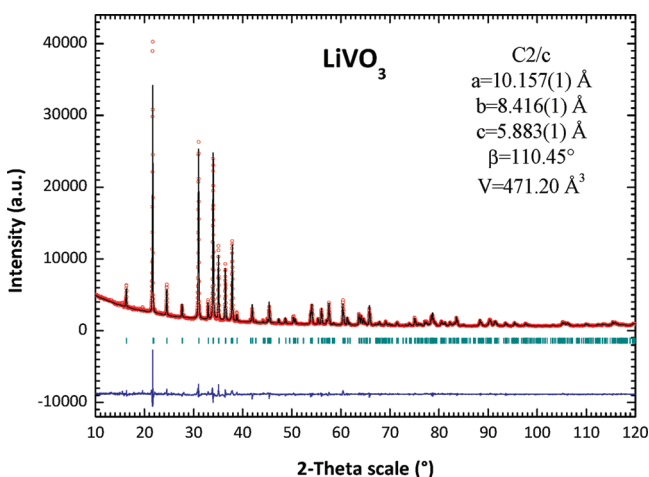


Figure 2. XRD pattern of  $\text{LiVO}_3$  as prepared.

material  $\text{LiVO}_3$  corresponds to a well-crystallized phase which can be indexed to the cell parameters  $a = 10.16 \text{ \AA}$ ,  $b = 8.415 \text{ \AA}$ ,  $c = 5.884 \text{ \AA}$ ,  $\beta = 110.50^\circ$ , and space group  $C2/c$ , as previously described.<sup>12</sup>

For the electrochemical study of  $\text{LiVO}_3$ , the charge and discharge profile were performed with a galvanostatic cycling at C/10 in the potential window 1.0–3.0 V versus  $\text{Li}/\text{Li}^+$  (Figure 3).

During the first discharge (labeled 1), which corresponds to the insertion of one lithium per formula, one observes a pseudo plateau suggesting a biphasic mechanism. This viewpoint is confirmed by the XRD analysis of the intermediate composition  $x = 0.6$ , which shows a mixture of two phases, the initial vanadate  $\text{LiVO}_3$ , and the final oxide  $\text{Li}_2\text{VO}_3$ . Note therefore that additional capacity is observed due to side reactions with the electrolyte occurring in the first reduction process. After the first cycle, a reversible process, characteristic of a solid solution process (i.e.,  $\text{Li}_{2-x}\text{VO}_3$  with  $0 \leq x < 1$ ), occurs (labeled 2–3). A reversible capacity of 0.9 Li/f.u. (253 (mA h)/g) is obtained at an average potential of 2.5 V.

The ex situ X-ray powder pattern taken at the end of the first discharge (Figure 4), that is, for  $\text{Li}_2\text{VO}_3$  composition, is completely different from that of the pristine phase  $\text{LiVO}_3$  (Figure 2). This pattern was refined in a cubic cell with a cell parameter,  $a = 8.23 \text{ \AA}$ , compatible with the space group  $Fd\bar{3}m$ , characteristic of the disorderer rock salt structure previously

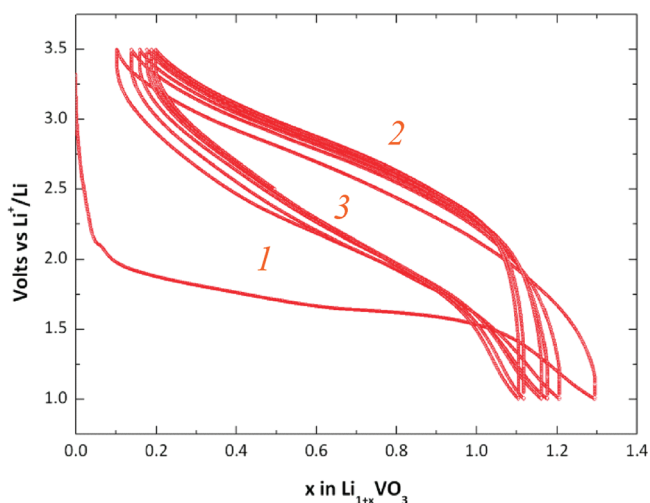


Figure 3. Potential composition curve of  $\text{LiVO}_3$  at C/10 rate.

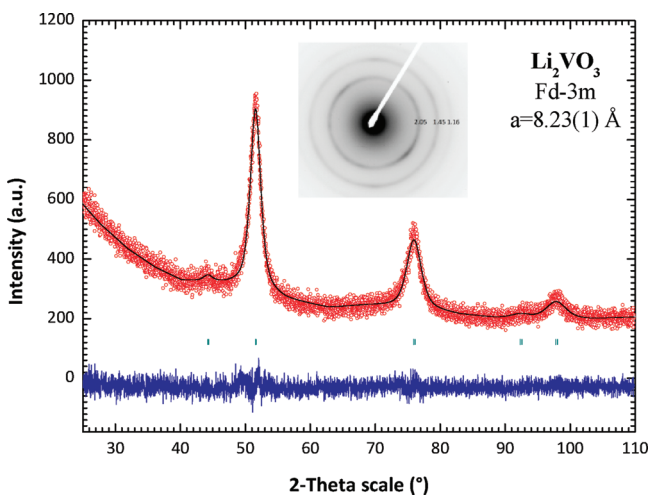


Figure 4. Ex situ X-ray patterns of the discharged phase  $\text{Li}_2\text{VO}_3$ . Inset: SAED showing the ring which characterizes the nanoscale phase.

observed for high pressure  $\text{LiVO}_2$ .<sup>14</sup> Note, however, that they reveal a strong amorphization of the sample, showing that the reconstructive reaction, corresponding to the irreversible transformation of the chain structure into the rock salt structure, occurs in the course of the first lithiation.

Interestingly, as the reversible process is a solid solution process, no further structural transformation is observed. Thus, the rock salt oxide,  $\text{Li}_2\text{VO}_3$ , can deintercalate–intercalate reversibly one Li per f.u. at the average potential of 2.5 V vs  $\text{Li}^+/\text{Li}$ , leading to a specific capacity of 253 (mA h)/g and a specific energy of 632 (W h)/kg (Figure 5).

These results show, for the first time, the possibility to deintercalate reversibly one Li per f.u. in a vanadium oxide, with the rock salt structures  $\text{Li}_2\text{VO}_3$ , without any structural transition, and for the sole  $\text{V}^{5+}/\text{V}^{4+}$  redox couple. Similarly, a structural transition is observed for other vanadium oxides  $\text{V}_2\text{O}_5/\text{Li}_3\text{V}_2\text{O}_5$  and  $\text{LiV}_3\text{O}_8/\text{Li}_5\text{V}_3\text{O}_8$ , leading to a rock salt structure. However, in those systems, the intercalation–deintercalation reaction requires two redox couples successively,  $\text{V}^{5+}/\text{V}^{4+}$  and  $\text{V}^{4+}/\text{V}^{3+}$ .

The performances of this new rock-salt-type  $\text{Li}_2\text{VO}_3$  oxide are comparable to those of the most recognized materials that are used as cathodes for Li-ion batteries (Figure 6). Clearly, one

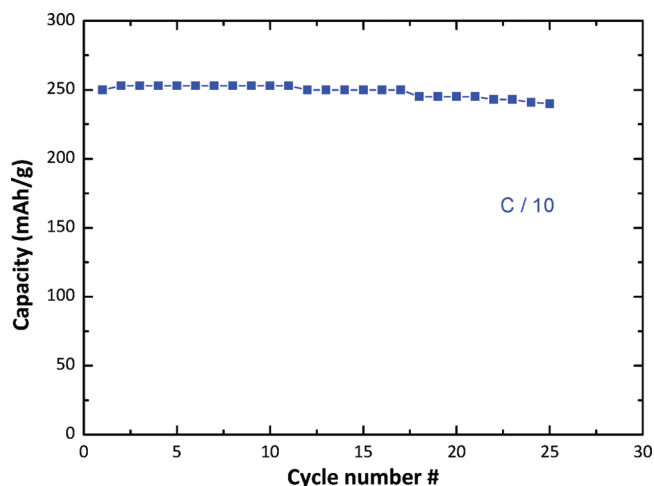


Figure 5. Capacity versus cycle number for  $\text{LiVO}_3$  at C/10.

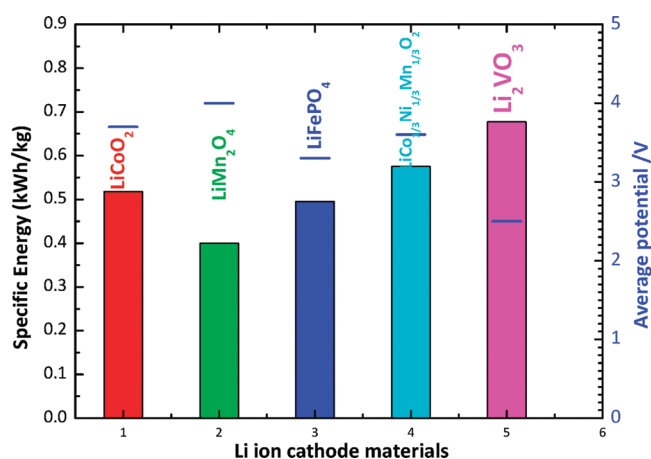


Figure 6. Specific energy ((kW h)/kg) and average potential vs  $\text{Li}^+/\text{Li}$  for several material used as cathode materials for Li ion batteries.

observes that despite its low redox potential (2.5 V vs  $\text{Li}^+/\text{Li}$ ) compared to other cathode materials (3.2 to 4 V),  $\text{Li}_2\text{VO}_3$  delivers a high specific energy, that is, 632 (W h)/kg to be compared to 400–550 (W h)/kg for the other.

In conclusion, a new candidate as electrode material for Li ion batteries,  $\text{Li}_2\text{VO}_3$  ( $\text{LiVO}_3$ ) with the rock salt structure, has been synthesized in the Li–V–O system. This oxide has the advantage of being very stable and easy to prepare from the in situ electrochemical reaction of  $\text{LiVO}_3$  synthesized at 500 °C. Moreover, this material could be directly synthesized by chemical intercalation using  $n\text{Bu-Li}$ . Importantly, its capacity is significantly higher than that of  $\text{Li}_2\text{V}_3\text{O}_8$  ( $\text{Li}_3\text{V}_3\text{O}_8$ ), and in contrast to  $\text{V}_2\text{O}_5$  ( $\text{Li}_3\text{V}_2\text{O}_5$ ), it can be used more easily as a reversible electrode since it involves only one redox couple  $\text{V}^{5+}/\text{V}^{4+}$ . Thus, it appears as a promising candidate for the elaboration of thin film electrodes for microbatteries.

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### Author Contributions

†The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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