

New electrode materials for lithium rechargeable batteries

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Abstract

In this paper, a contribution to the search of new electrode materials for lithium batteries is reported. First, we will present the electrochemical behavior of an Aurivillius-type phase with the composition $\text{Bi}_4\text{V}_2\text{O}_{11}$. This oxide may be used as cathode material (390 A h/kg) if the voltage is not so low (average voltage 1.6 V). On the other hand, if $\text{Bi}_4\text{V}_2\text{O}_{11}$ is reduced down to 0.5 V, it reacts with 28 Li ions per formula unit. Considering only the low voltage region, $\text{Li}_{28}\text{Bi}_4\text{V}_2\text{O}_{11}$ could be a candidate to anode material (360 A h/kg at 0.7 V). Our research has also been directed towards the applications of several types of titanium oxides in lithium batteries. Among these compounds, we present the results for $\text{K}_x\text{Ti}_8\text{O}_{16}$ and $\text{Li}_2\text{Ti}_3\text{O}_7$. The best results are those obtained from the ramsdellite $\text{Li}_2\text{Ti}_3\text{O}_7$: the large reversibility, low polarization and relatively high capacity (235 A h/kg) make this compound a promising material as negative electrode for lithium ion cells. However, the relatively high average potential, close to 1.4 V, would reduce considerably the performance of a rocking-chair battery using this ramsdellite instead of carbon. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The development of new materials useful as electrode materials in rechargeable lithium cells has received more than a considerable attention in the last few years. First, the quest was mostly devoted to cathode materials. It seems that the use of very high voltage materials may compensate the energy loss originated if an intercalation compound instead of lithium is used as the negative electrode. However, the high voltage cathodes that are being used, studied and modified are mainly the well-known LiMn_2O_4 , LiNiO_2 and LiCoO_2 , the latter being the only one compound used in commercial batteries [1]. Besides, researchers look for new anodes to improve the performance of the cells using carbonaceous compounds as the negative electrode. Alloys and other type of compounds, e.g., oxides, chalcogenides and nitrides, have received a lot of attention. Some of them can be considered as good negative electrode candidates since they have high specific

parameters as is the case of $\text{Li}_{1+x}\text{MVO}_4$ [2] and $\text{Li}_{3-x}\text{M}_x\text{N}$ [3], which have been recently reported.

The amount of work done on such research has been huge. Searching for completely new compounds, modification of the better known electrodes, etc., have been mostly done on the base of, let us say, one's particular intuition. If we think about the materials that are being presently intensively studied and either commercially used or proposed to be used, we will face a set of really very old references [4–6] for example. In this sense, the searching for new electrode materials seems to be a journey to nowhere. However, very interesting materials have been recently reported, that, although quite related to the four volts materials, show good performances at much higher voltage. This is for example the case of the compound $\text{Li}_2\text{Mn}_3\text{CoO}_8$ which can be cycled between 4 and 5.3 V [7]. On the other hand, a very good complement has been recently developed as a tool for scientists on this field. First-principles calculations have been proposed as a guide to predict the energy, and hence, the average potential of both reactants and products of an intercalation reaction. [8].

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In the next pages, the work done on two different types of compounds aiming for new electrode materials is reported.

First, we will refer to the Aurivillius like-phase, α - $\text{Bi}_4\text{V}_2\text{O}_{11}$. Although only the electrochemical behavior of this compound is presented, a more complete study of the intercalation chemistry of this layered material with lone pairs of electrons directed to the interlayered space has been done [9].

Afterwards, we will describe the electrochemical behavior of different titanium oxides in which $\text{Ti}^{4+}/\text{Ti}^{3+}$ is coordinated to six oxygen atoms in an octahedral environment. In particular, we will mention the results obtained from an electrochemical study of the ramsdellite $\text{Li}_2\text{Ti}_3\text{O}_7$ and the $\text{K}_x\text{Ti}_8\text{O}_{16}$ bronzes.

2. Experimental aspects

All the starting host materials have been prepared through the standard ceramic method using the appropriate conditions as described in Refs. [10–12]. The structural characterization was made by means of X-ray powder diffraction (Siemens D-5000 and Philips X'Pert) with Ni-filtered Cu K α radiation. The electrochemical experiments were performed in Swagelok cells with the following configuration: Li/LiClO_4 (1 M) in EC + DEE (1:1)/host material + carbon black + binder. However, the more recent experiments were made using LiPF_6 (1 M) in EC + DMC (2:1) as the liquid electrolyte, provided by Merck. The cells were controlled using a MacPile system [13].

3. Results and discussion

3.1. $\text{Bi}_4\text{V}_2\text{O}_{11}$ and related compounds

A voltage-composition plot for a cell using $\text{Bi}_4\text{V}_2\text{O}_{11}$ as the positive electrode is shown in Fig. 1. It can be seen

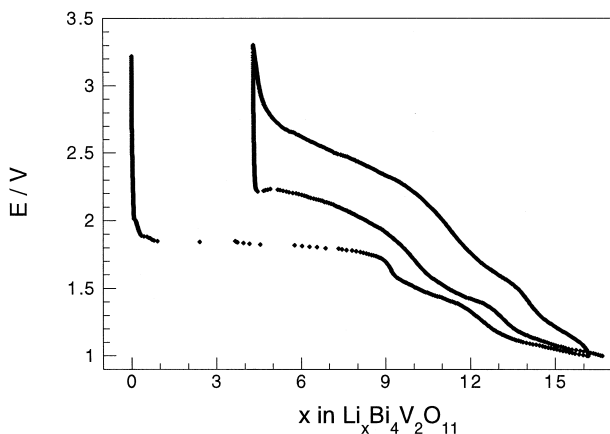


Fig. 1. Typical voltage-composition plot obtained between 3.3 and 1 V for the electrochemical lithium intercalation in $\text{Bi}_4\text{V}_2\text{O}_{11}$. The data were collected from a cell with the configuration $\text{Bi}_4\text{V}_2\text{O}_{11}/\text{LiClO}_4$ (1 M) in EC + DEE (50:50)/Li. The current density applied was $0.06 \text{ mA}/\text{cm}^2$.

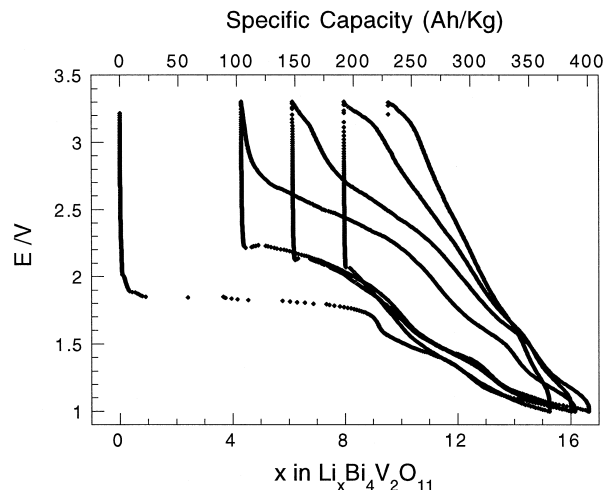


Fig. 2. Cycling behavior of a cell $\text{Bi}_4\text{V}_2\text{O}_{11}/\text{LiClO}_4$ (1 M) in EC + DEE (50:50)/Li under a current density of $0.06 \text{ mA}/\text{cm}^2$ between 3.3 and 1 V.

that during the first reduction, down to 1 V, the oxide reacts with 16 lithium ions. However, during the first oxidation, only approximately 12 lithium ions can be removed. These lithium ions can be later on reversibly inserted, as it is deduced from both the shape and the length of the second reduction curve. The specific capacity calculated from the first reduction (390 A h/kg) is reduced in the second discharge to 290 A h/kg. However, the most important problem for this material is the fading of capacity upon cycling and the rapid increase of cell polarization (see Fig. 2).

Concerning the loss of capacity between the first and second discharge, this does not vary when cells are discharged limiting the degree of insertion to 4 and 9.5 lithium ions per formula, respectively. We think that an irreversible transformation occurs in $\text{Bi}_4\text{V}_2\text{O}_{11}$ just for the very first lithium that reacts in which the Bi lone pair seems to play a relevant role [9,14].

The behavior of a cell bearing α - $\text{Bi}_4\text{V}_2\text{O}_{11}$ as the positive electrode discharged at a much lower voltage is represented in Fig. 3. Between 3.3 and 0.5 V, α - $\text{Bi}_4\text{V}_2\text{O}_{11}$ reacts with 28 lithium ions per formula during the first discharge. The charge of the cell allows the extraction of almost 20 lithium ions. Since the extraction process above 1.2 V is affected by a high polarization, the useful range for applications would be 1.2–0.5 V. In this voltage range, the oxide may be used as anode material developing a specific capacity of about 360 A h/kg of electrode material at an average voltage of 0.7 V. Fig. 4 shows the first cycles of a cell discharged down to 0.5 V and then charged up to 1.2 V. The reversibility is high and much better in comparison to cells discharged down to 1 V (see Fig. 2).

3.2. Some titanium oxides

We have studied the electrochemical behavior of two titanium oxides in which the arrangement of the Ti–O₆

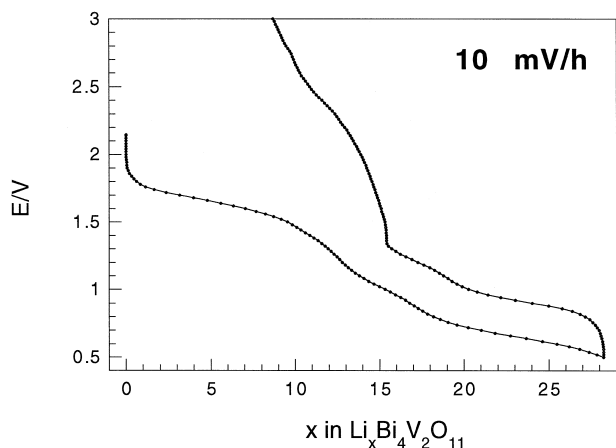


Fig. 3. Typical voltage-composition plot obtained from a potentiostatic discharging-charging cycle of a cell $\text{Bi}_4\text{V}_2\text{O}_{11}/\text{LiClO}_4$ (1 M) in EC + DEE (50:50)/Li at 10 mV/h between 3.3 and 0.5 V.

strings gives rise to tunnels of different size; $\text{K}_{1.55}\text{Ti}_8\text{O}_{16}$ presents a hollandite-like structure, whereas $\text{Li}_2\text{Ti}_3\text{O}_7$ is a member of the ramsdellite family.

In the case of $\text{Li}_2\text{Ti}_3\text{O}_7$, the amount of lithium that is inserted under open-circuit-voltage (ocv) conditions down to 1 V (see Fig. 5) represents a high theoretical capacity (240 A h/kg) [15]. Reversibility and cycling behavior in this potential range are excellent, as can be seen in Fig. 6. Furthermore, a very low polarization is observed in this experiment performed at a current density of 0.16 mA/cm². At higher current rates, the ramsdellite maintains acceptable values of specific capacity (129 A h/kg for C/10) in view of its possible application as anode material. Although we have not yet performed long-life cycling behavior experiments, the structural characterization has shown that the phase with the maximum lithium

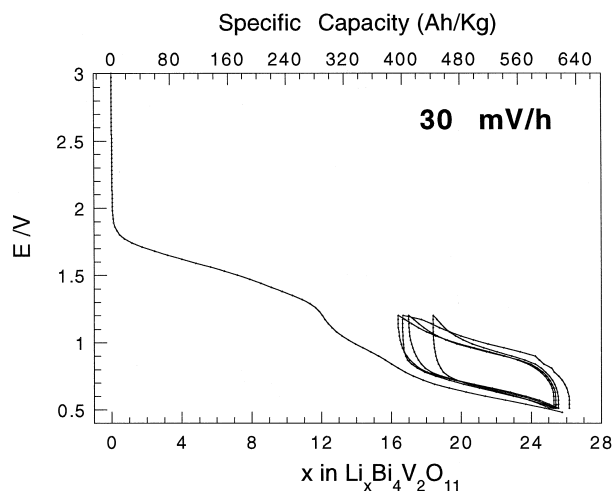


Fig. 4. Behavior of a cell $\text{Bi}_4\text{V}_2\text{O}_{11}/\text{LiClO}_4$ (1 M) in EC + DEE (50:50)/Li discharged down to 0.5 V and cycled afterwards at 30 mV/h between 0.5 and 1.2 V.

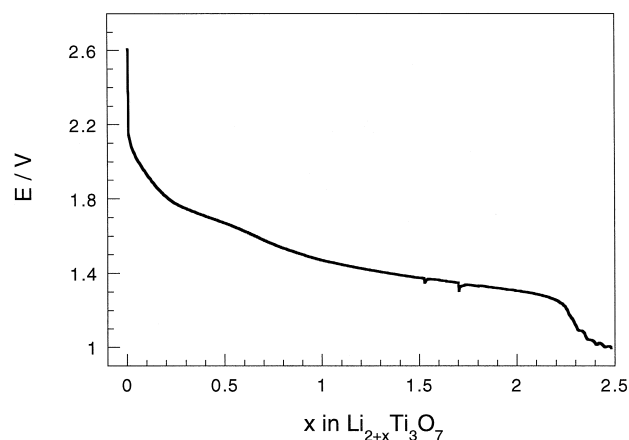


Fig. 5. Open-circuit-voltage experiment carried out in a cell with the configuration $\text{Li}_2\text{Ti}_3\text{O}_7/\text{LiClO}_4$ (1 M) in EC + DEE (50:50)/Li.

content, $\text{Li}_{4.2}\text{Ti}_3\text{O}_7$, possesses a ramsdellite-related structure which undergoes only a 2% volume change with respect to the initial compound [9]. Since this variation is very low, even compared with 9.4% occurring in the intercalation process of C to get LiC_6 [16] which is actually the acting anode material of the commercial rocking-chair battery, the cycling behavior of $\text{Li}_2\text{Ti}_3\text{O}_7$ is very promising. Finally, we want to recall that it is not possible to take advantage of the two lithium ions per formula in $\text{Li}_2\text{Ti}_3\text{O}_7$ for improving the cell capacity, as Ti is already in its highest oxidation state, 4+, and extraction of lithium from this compound is not feasible.

Another way taken to obtain an open Ti–O framework structure has been potassium extraction from the ternary oxide bronzes $\text{K}_x\text{Ti}_8\text{O}_{16}$, following the procedure described by Latroche et al. [17]. With this aim, we have prepared a ‘starting’ $\text{K}_x\text{Ti}_8\text{O}_{16}$ bronze which, taking into

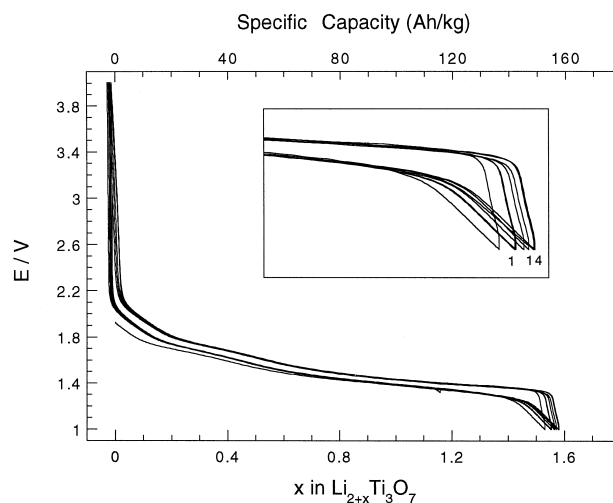


Fig. 6. Cycling behavior of a cell $\text{Li}_2\text{Ti}_3\text{O}_7/\text{LiClO}_4$ (1 M) in EC + DEE (50:50)/Li at a current density of 0.16 mA/cm².

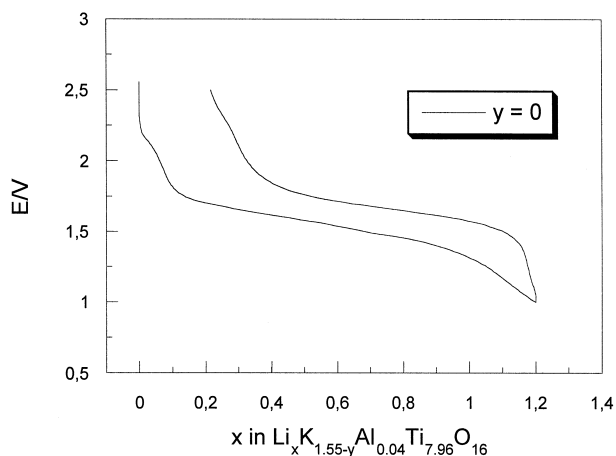


Fig. 7. Open-circuit-voltage experiment carried out in a cell with the configuration $\text{K}_{1.55-y}\text{Al}_{0.04}\text{Ti}_{7.96}\text{O}_{16}/\text{LiClO}_4$ (1 M) in EC+DEE (50:50)/Li ($y=0$).

account the elemental chemical analysis, should be formulated as $\text{K}_{1.55}\text{Al}_{0.04}\text{Ti}_{7.96}\text{O}_{16}$. The electrochemical lithium intercalation experiment for the starting bronze (Fig. 7) shows that about 1 Li/formula can be intercalated under ocv conditions with a specific capacity of 35 A h/kg [18].

By treating a sample of $\text{K}_{1.55}\text{Al}_{0.04}\text{Ti}_{7.96}\text{O}_{16}$ under reflux in a solution of sulfuric acid and hydrogen peroxide (50:50) as recently described [17], we obtained materials of composition $\text{K}_{1.55-y}\text{Al}_{0.04}\text{Ti}_{7.96}\text{O}_{16}$ ($y=1.27$ and 1.53). The latter represents the practically potassium-free TiO_2 polymorph labeled as $\text{TiO}_2(\text{H})$. Once some potassium ions have been removed from the tunnel structure of the starting bronze, the quantity of lithium that can be inserted increases to rather high values (Fig. 8). Therefore, the

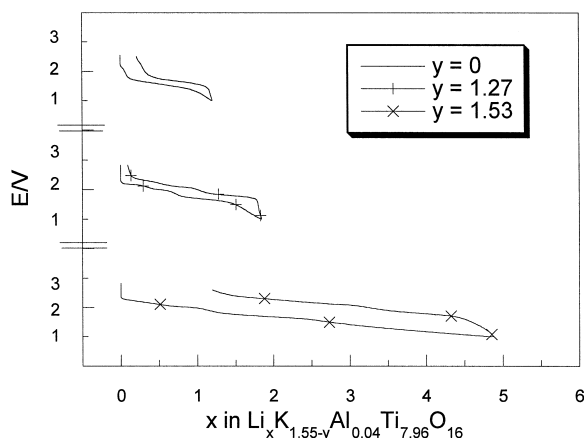


Fig. 8. Typical voltage-composition plot obtained between 3.0 and 1 V for the electrochemical lithium intercalation in several $\text{K}_{1.55-y}\text{Al}_{0.04}\text{Ti}_{7.96}\text{O}_{16}$ compounds; $y=0$ (starting material), $y=1.27$ and 1.53 . The data were collected from a cell with the configuration $\text{K}_{1.55-y}\text{Al}_{0.04}\text{Ti}_{7.96}\text{O}_{16}/\text{LiPF}_6$ (1 M) in EC+DMC (2:1)/Li. The current density applied was 0.06 mA/cm^2 .

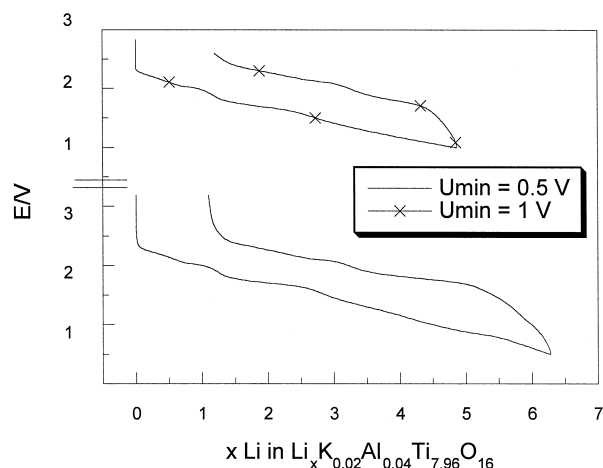


Fig. 9. Typical voltage-composition plot for the electrochemical lithium intercalation in $\text{K}_{0.02}\text{Al}_{0.04}\text{Ti}_{7.96}\text{O}_{16}$ obtained from 3.0 down to 1 and 0.5 V, respectively. The data were collected from a cell with the configuration $\text{K}_{0.02}\text{Al}_{0.04}\text{Ti}_{7.96}\text{O}_{16}/\text{LiPF}_6$ (1 M) in EC+DMC (2:1)/Li. The current density applied was 0.25 mA/cm^2 .

remaining potassium ions play an important part in the amount of inserted lithium.

The capacity for the most extracted compound can even be driven to 260 A h/kg, if the cut-off limiting voltage is set to 0.5 V without any change in the cell reversibility (Fig. 9). Some loss of reversibility is observed between the first and second discharge, although a fairly good cyclability is maintained after the following consecutive cycles (Fig. 10). This initial loss may be due to the presence of intercalated water which has been detected to reach a 0.5% in total weight. Actually, we are studying the dehydration of these samples in view of their electrochemical behavior. Results will be published elsewhere.

Taking into account these results, the material of composition $\text{K}_{0.02}\text{Al}_{0.04}\text{Ti}_{7.96}\text{O}_{16}$ may also be useful as anode material in rocking-chair batteries.

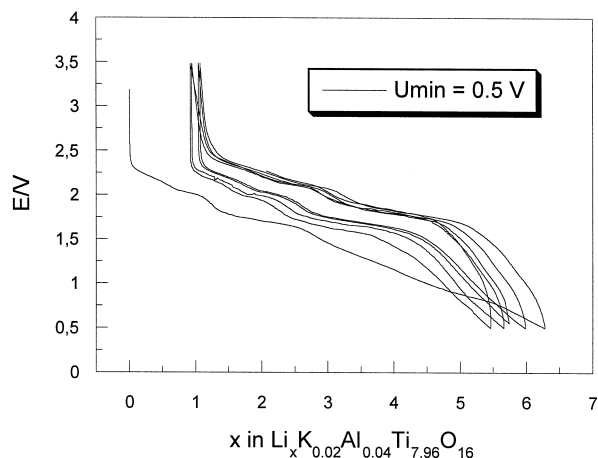


Fig. 10. Cycling behavior of a cell $\text{K}_{0.02}\text{Al}_{0.04}\text{Ti}_{7.96}\text{O}_{16}/\text{LiPF}_6$ (1 M) in EC+DMC (2:1)/Li at a current density of 0.25 mA/cm^2 between 3 and 0.5 V.

4. Conclusions

We have shown that the compounds $\text{Bi}_4\text{V}_2\text{O}_{11}$, $\text{Li}_2\text{Ti}_3\text{O}_7$ and $\text{K}_x\text{Ti}_8\text{O}_{16}$ may be used as electrode materials for lithium batteries.

The Aurivillius phase $\text{Bi}_4\text{V}_2\text{O}_{11}$ would find its better performance as anode material in rocking-chair batteries. Nevertheless, a previous deep discharge is needed in order to obtain the lithiated compound $\text{Li}_{28}\text{Bi}_4\text{V}_2\text{O}_{11}$, which reversibly deintercalates 16 lithium ions in the voltage range 1.2–0.5 V. One should not forget that this process would imply a substantial raise in production costs of the real active material, and it would be a disadvantage to compete with already commercialized anode materials.

On the other hand, for the titanium oxides, $\text{Li}_2\text{Ti}_3\text{O}_7$ and $\text{K}_{0.02}\text{Al}_{0.04}\text{Ti}_{7.96}\text{O}_{16}$, as anode material for rocking-chair batteries, all the lithium ions intercalated during the first charge of the cell are afterwards used in its working operation. The maximum specific capacities which have been obtained during the first discharge of lithium cells, down to 1 V, are 240 A h/kg for $\text{Li}_2\text{Ti}_3\text{O}_7$ and 205 A h/kg for $\text{K}_{0.02}\text{Al}_{0.04}\text{Ti}_{7.96}\text{O}_{16}$ at an average voltage close to 1.4 V in both cases.

Although the $\text{K}_{0.02}\text{Al}_{0.04}\text{Ti}_{7.96}\text{O}_{16}$ material requires further detailed studies in order to optimize its performance, the ramsdellite-type $\text{Li}_2\text{Ti}_3\text{O}_7$ with a very low polarization and high reversibility is a promising candidate as anode material in rocking-chair batteries. Since the substitution of carbon by $\text{Li}_2\text{Ti}_3\text{O}_7$ represents an energy loss due to the higher average voltage of the latter with respect to carbon, we are presently developing 5 V cathode materials.

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