



Revisiting the relevance of using a constant voltage step to improve electrochemical performances of Li-rich lamellar oxides



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HIGHLIGHTS

- The relevance of using a CVS has been evaluated for Li-rich lamellar oxides.
- A CVS at high potential favors defects occurrence and increases voltage fading.
- To keep a CVS for industrial application, the cut-off voltage must be decrease.

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ABSTRACT

A Li-rich lamellar oxide was cycled at high potential and the relevance of using a constant voltage step (CVS) at the end of the charge, needed for industrial application, was investigated by electrochemical performance, X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM). Electrochemical studies at 4.7 and 4.5 V with and without CVS showed that capacity and voltage fading occurred mostly when cells operated at high potential. After cycling, 3D-type defects involving transition metals trapped in lithium layer were observed by HRTEM into the electrode bulk. These defects are responsible for the voltage fading. XRD microstrain parameter was used to evaluate defects rate in aged materials subjected to a CVS, showing more 3D-type defects when cycled at 4.7 V than at 4.5 V.

The time spent at high potential at the end of the charge as well as the value of the upper potential limit, are both relevant parameters to voltage decay. The use of a CVS at the end of the charge needs at the same time, a reduced upper potential window in order to minimize 3D-type defects occurrence. Unfortunately, this approach is still not sufficient to prevent voltage fading.

1. Introduction

The increasing demand for energy as well as the need to reduce the environment pollution requires an important development of systems to store energy such as batteries. The commercial Li-ion batteries used today need to increase the amount of stored energy, meaning a higher energy density in order to meet energy challenges [1–3].

With the aim to increase the performance of marketable batteries, many groups were looking for new materials in order to elaborate better positive electrodes derived from the reference material LiCoO₂ [4]. Therefore a new family of compounds has been proposed: the Li-rich lamellar materials Li_{1+x}(M)_{1-x}O₂ also described as a xLi₂MnO₃·(1-x)LiMO₂ with M = Mn, Ni, Co, Cr, Fe, ... [5–12].

These compounds have been extensively studied during the last decade because of their large specific capacities (over 250 mAh.g⁻¹). The large capacity can be explained by a significant participation of oxygen as an electron donor. It has been proposed in the literature that a part of the charge compensation during cycling can be partially explained by oxygen departure from surface, which could contribute to the significant irreversible capacity observed during the first cycle [13–15]. However, the great part of charge compensation can also be explained by redox activation of the oxygen from the Li₂MnO₃ acting in a reversible manner [16–19].

Nevertheless, a significant decrease in the operating voltage occurs in cycling which results in a large decrease of the energy density. To explain this phenomenon which extends during cycling, several authors

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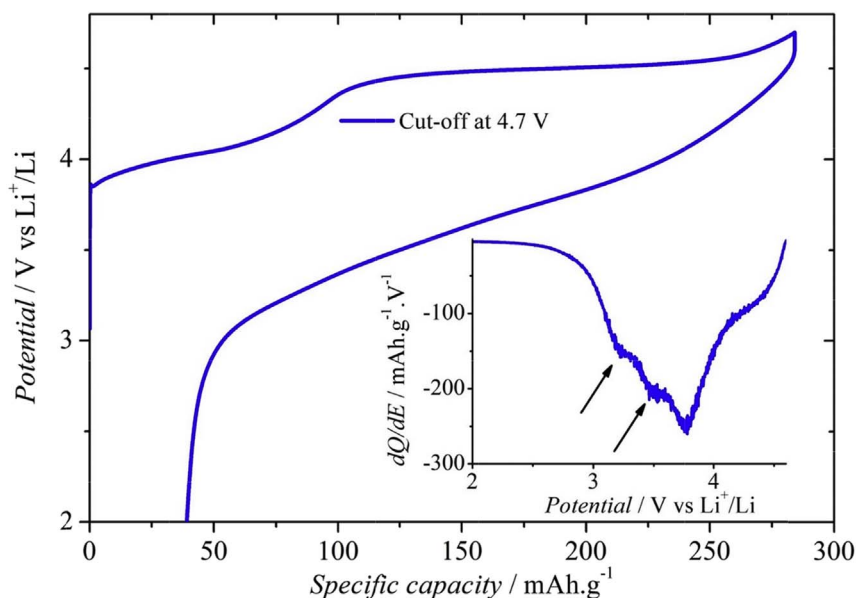


Fig. 1. Activation cycle between 2 and 4.7 V. The corresponding derivative curve of discharge process is shown as an inset. Two electrochemical phenomena are observed at lower potential (black arrows).

suggest a transformation of the material from a lamellar phase into a spinel-type phase by migration of transition metals into lithium layers [20,21].

In fact, Li-rich lamellar oxides could be marketable as positive electrodes only if it is possible to obtain a large capacity without decreasing the operating voltage in order to get a maximum energy density. Consequently, many groups tested several routes to prevent voltage fading [22–24]. Thus, Sathiya et al. [25] has shown that an element with a larger ionic radius in the transition metal layer could limit the decrease of the operating voltage. Peralta et al. [26] also showed a relationship between the decrease of the operating voltage and the upper limit of the voltage window during cycling. They showed that limiting the upper potential window below 4.3 V reduced the voltage decay.

Furthermore, industrial companies build batteries in such a way that a constant voltage step (CVS) is applied at the end of the charge in order to limit the risk of an important decrease of the capacity due to only one cell in the battery. As a structural modification of these materials occurs at high potential, it seems important to evaluate the effect of a CVS on electrochemical performances. Indeed, in this work, we studied the influence on voltage decay of (i) the upper limit of the voltage window, (ii) the cycling rate and (iii) the use of a CVS at the end of the charge. The evolution of the electrode structure during aging was characterized by *ex-situ* X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM) and *operando* XRD.

2. Experimental

Synthesis and chemical characterizations of starting powders were made by our industrial partner. The Li-rich electrode $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ was used as active material in this work. XRD pattern and corresponding Le Bail refinement (Fig. S1 and Table S1) attested to the starting material is single-phased. Moreover, SEM image (Fig. S2a) shows a submicrometric powder and TEM image (Fig. S2b) provides evidence of an ordered stacking of the atomic layers before cycling. Electrodes were shaped on an aluminum foil of an ink formed by a mixture of the active material, a percolating carbon and a polymer binder Polyvinylidene fluoride (PVDF) with the corresponding ratio of 92/4/4. The loading of the electrode was evaluated at 12 mg cm^{-2} . Before assembling the battery, electrodes were dried overnight at 120°C in a Büchi oven. The Swagelok-type cells were assembled in a glove box filled with argon gas, with a disc of Li as a negative electrode,

two Celgard separators and some electrolyte (1 M LiPF_6 in a mixture of four organic solvents). Galvanostatic charge-discharge cycles were performed on MPG (Bio-Logic) equipment. The conditions of tests will be described in the next section. We calculate the average operating voltage in discharge as the ratio between the energy and the capacity of the cell obtained at the end of the discharge. For *ex-situ* analysis, electrodes were recovered in glove box, washed in Dimethyl carbonate (DMC), dried and analyzed.

Ex-situ room temperature XRD data were obtained using a Bruker “D8 Advance” powder diffractometer operated in Bragg-Brentano geometry with a Cu anode sealed x-ray tube and a focusing Ge(111) primary monochromator (selecting the $\text{Cu K}_{\alpha 1}$ radiation; $\lambda = 1.540598 \text{ \AA}$). We used a 1-D silicon-strip position sensitive detector (“LynxEye” detector) with an active data collection angle of $3.7^\circ 2\theta$ (goniometer radius: 217.5 mm). Diffractometer settings were 40 kV, 40 mA, $10 - 90^\circ 2\theta$, step size $0.2^\circ 2\theta$ and 7 s counting per step. Le Bail refinements were carried out using JANA 2006 software [27] with the fundamental parameters method to study directly the evolution of the strain parameter for each sample.

The *operando* XRD study was conducted at the synchrotron radiation facility SOLEIL (France) on CRISTAL beamline, using an *in-situ* cell [28]. The wavelength of the beam impinging on the sample was set to $\lambda = 0.6687 \text{ \AA}$, and each XRD pattern was obtained every 4 min between $2\theta = 6$ and 40° using an Image plate detector (MAR345 from Marresearch) in transmission mode.

A transmission electron microscope (TEM), Hitachi HNAR9000, operating at 300 kV was used to obtain high-resolution images and electron diffraction patterns. The image processing was performed using the software Gatan digital micrograph. JEMS program was used for image calculations.

3. Results and discussions

3.1. Electrochemical behavior

First cycling conditions were adapted to obtain the maximum of capacity from the electrode. The activation cycle, shown in Fig. 1, is done between 2 and 4.7 V at a low rate C/20. As already described by several groups, the plateau observed after 4.3 V is related to lithium removal with oxidation of oxygen ions [18,29]. This phenomenon is closely related to the Li_2MnO_3 -type order existing in the starting material. During the discharge, new phenomena appeared at low potential around 3 and 3.5 V (see inset in Fig. 1). According to the literature [18],

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