



Role of the composition of lithium-rich layered oxide materials on the voltage decay



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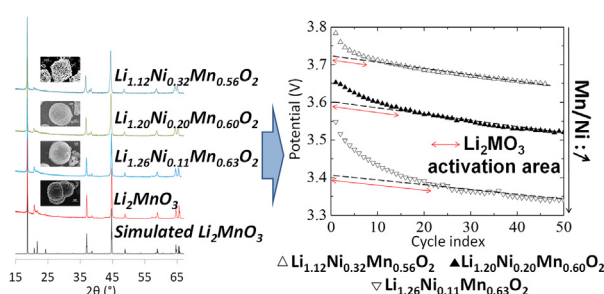
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HIGHLIGHTS

- Electrochemical behavior of four lithium-rich layered materials have been compared.
- Materials with different Mn/Ni ratios were synthesized using coprecipitation route.
- Whatever the compositions, same phenomena are involved.
- Materials with high Mn content evolve faster than high Ni content materials.
- The potential decay is provoked by at least two phenomena.

GRAPHICAL ABSTRACT



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ABSTRACT

Lithium-rich layered oxide is known to be one of the most promising positive electrode materials for high energy Li-ion batteries. Some publications report specific capacities higher than 250 mAh/g but the fade of the average potential during electrochemical cycling is an important drawback for commercial use of this material. The objective of this work is to study the origin of this potential decay during cycling of lithium-rich compounds. For this purpose, the electrochemical behavior of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ (with $x = 1, 0.7, 0.5, 0.27$) materials synthesized using coprecipitation route have been compared. For this study, complete or partial charge and discharge cycles have been performed in the 2.5 V–4.8 V voltage range. The results can be briefly summarized as follows: the potential decay is mainly provoked by several phenomena occurring at low potential, this growth being induced by the charging of lithium-rich at high voltage (>4.15 V). Whatever the compositions, same phenomena are involved, only the kinetics is modified.

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1. Introduction

Energy storage is one of the most important challenges of the energy transition process. In this context, lithium ion batteries (LIBs) have been widely developed in the last two decades. Since the introduction of LIBs in 1991 by Sony, LiCoO_2 is still the most

common material on the LIBs market [1]. With the rapid development of hybrid electric vehicles (HEV) and electric vehicles (EV), it is necessary to find new cathode materials to overcome the drawbacks of LiCoO_2 : high cost, toxicity, safety problems and limited energy density. Researchers are working on cobalt-poor materials which could reach a higher capacity and/or a higher voltage (nickel manganese cobalt lithium layered oxides named NMC, spinel oxides, olivines and lithium-rich...). Among them, lithium-rich materials have very high practical energy densities and very high capacities (>250 mAh/g). Besides their electrochemical performances, the layered-layered ($x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$) family is economically attractive due to its composition mainly rich in manganese which is cheaper than cobalt. From a structural point of view, the lithium-rich layered materials can be regarded as a composite material built of LiMO_2 and Li_2MO_3 domains ($M = \text{Mn}, \text{Ni}$) [2]. The high specific capacities of these materials are attributed to the reversible capacity coming from the redox activity of cations in the LiMO_2 component and to an additional capacity corresponding to the electrochemical activation of the Li_2MO_3 component above 4.4 V [3]. Li_2MO_3 part is transformed into an electrochemically active component due to the simultaneous removal of both lithium and oxygen from the lattice during the initial charging process. However the electrochemical activation process of lithium-rich materials is not really understood, especially the oxygen role during the first charge. Armstrong et al. [4] observed a gas release during the first charge attributed to the oxidation of O^{2-} anions to O_2 which is irreversibly extracted from the structure. Meanwhile Koga et al. [5] and Sathiya et al. [6] have shown that a reversible O^{2-}/O^- redox process could also occur in these materials. These transformations in the structure generate a high capacity but induce also important drawbacks: a large irreversible capacity during the first cycle and the progressive fade of the average cell voltage during the cycle life [7,8]. The irreversible capacity observed during first cycle could be reduced by surface treatment of lithium-rich using coatings with materials which are active during the discharge step [9]. Nevertheless, these surface treatments do not solve the potential decay [10]. This phenomenon is not yet understood, but its effect on cell performances is dramatic as it leads to a continuous energy density loss during cycle life, and difficulties to adapt battery management systems (BMS) to this technology.

Several explanations have been proposed. The most cited and admitted reason is the migration of the transition metal cations that induces a slow transformation from a layered structure to a “spinel type” one [2,8,11,12]. Moreover, Gallagher et al. [13] suggested a direct correlation between the voltage decay and the observed 1 V hysteresis. According to them, a small quantity of cations can reversibly migrate, and are at the origin of the hysteresis between high and low potentials. However, a part of the transition metal cations irreversibly migrates and causes the potential fade. Yu et al. [14] suggested that voltage decay is correlated to the continuous activation of the residual Li_2MO_3 component. Recently our group showed that several mechanisms have to be taken into account in order to explain the voltage fade [2,15]. We showed that a spinel like phase is mainly formed during the first cycle at the surface of the material and does not evolve significantly during cycling and we highlighted a mechanism where manganese cations migrate more quickly than the nickel ones - the migration being activated by the existing Li vacancies formed after the first charge - and causes segregation and densification within the lithium-rich material. We think that this mechanism could participate in the potential decay.

The present study belongs therefore to the same context. We aim to complete and to confirm our previous conclusions. Owing to the importance of the relationship between the structure and

electrochemical performance of lithium-rich materials, it is necessary to deeply understand and precisely control their composition. For this, we synthesized four lithium-rich materials, with different Mn/Ni ratios in the aim to understand the Mn role on the voltage decay.

2. Experimental

2.1. Synthesis

$x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ (with $x = 1, 0.7, 0.5, 0.27$) powders were synthesized by a coprecipitation procedure using commercial reactants from Sigma Aldrich®: nickel sulfate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 99%), manganese sulfate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$, 99%), lithium carbonate (LiCO_3 , 99%) and sodium carbonate (Na_2CO_3 , 99.95%). All the reactants were used without further purification.

Lithium-rich materials (Table 1) were synthesized using the same experimental conditions. Only the Mn/Ni ratios were adapted in order to obtain the target composition. For example, the synthesis protocol of $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ material can be summarized as follows: 0.125 mol of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and 0.375 mol of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ were mixed in 250 mL of water. In another container, 2 mol of Na_2CO_3 and 1.429 mol of NH_4OH were mixed in 1 L of deionized water. The transition metal ion solution was pumped directly into the CSTR reactor and the pH was kept at 7.5 during the whole synthesis by injecting the carbonate solution. Then, the final solution of the CSTR was aged for 7 h. Afterward, the carbonate of nickel and manganese ($\text{Ni}_{0.25}\text{Mn}_{0.75}\text{CO}_3$) was recovered by filtration. The product was washed several times with hot water in order to remove residual sodium and sulfate species and finally, the carbonate was dried in an oven at 393 K during one night. To obtain the final $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ material, $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{CO}_3$ was intimately mixed with an excess (3.3%) of lithium carbonate (Li_2CO_3) and the mixture was fired at 900 °C during 24 h.

2.1.1. Characterization

Purities of all products were controlled by X-ray diffraction using a Brüker AXS D8 diffractometer, equipped with a Cu anticathode.

Morphology of the products were determined by scanning electron microscopy using a LEO 1530 FE-SEM microscope equipped with a field electron gun.

The electrochemical characterizations were done using coin-type R2032 cells that consisted of a cathode and a lithium foil anode separated by a Celgard® 2400 porous polypropylene film and a Viledon® separator. Cathodes were fabricated by coating a slurry of 80 wt% active materials, 10 wt% carbon and 10 wt% PVDF in N-methyl-2-pyrrolidone as a solvent on aluminum foil. The electrolyte was 1 mol/L LiPF_6 in EC/PC/DMC in a volume ratio of 1/1/3. Coin cells were assembled in an argon-filled glove box and were cycled on an Arbin® tester in galvanostatic mode. Charge and discharge tests were performed at the current discharge of 31.6 mA/g (C/10) in the voltage range of 2.5 V–4.8 V at room temperature. All the potentials in this study are given versus Li/Li^+ and the average

Table 1
Link between one and two components notation.

x	Two components notation	Compact notation
1.00	Li_2MnO_3	Li_2MnO_3
0.70	$0.7\text{Li}_2\text{MnO}_3 \cdot 0.3\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$	$\text{Li}_{1.26}\text{Ni}_{0.11}\text{Mn}_{0.63}\text{O}_2$
0.50	$0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$	$\text{Li}_{1.20}\text{Ni}_{0.20}\text{Mn}_{0.60}\text{O}_2$
0.27	$0.27\text{Li}_2\text{MnO}_3 \cdot 0.73\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$	$\text{Li}_{1.12}\text{Ni}_{0.32}\text{Mn}_{0.56}\text{O}_2$

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