

An active Li-Mn-O compound for high energy density Li-ion batteries

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Due to their low weight, high energy densities and long cycle life, the battery scientific community is still trying to develop new high capacity cathodes materials in order to increase the energy density of storage devices [1].

After a composition screening, a new material family has been discovered in the Li-Mn-O system and has been investigated as potential new material for Li-ion batteries to replace conventional NMC materials ($\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$) [2]. In this study, we report for the first time the synthesis, structural and electrochemical characterizations of a new non-lamellar oxide with the highest capacity observed ever before in the Li-Mn-O system. This new patented [3] material with the composition of $\text{Li}_4\text{Mn}_2\text{O}_5$ shows a discharge capacity of 300 mAh/g. It is a rock-salt type nanostructured material, prepared by a direct mechanochemical synthesis. The typical crystallite size is about 5-10nm (from Transmission electron microscopy TEM and electron diffraction ED). The ring ED pattern of this individual phase can be indexed on the cubic $Fm-3m$ structure, with a rock-salt cell parameter of $a=4.16\text{\AA}$, according to Rietveld refinement.

The electrochemical performances were performed at a C/20 rate, and show a reversible discharge capacity about 300 mAh/g. A gradual increase in the cut-off voltage up to 4.8V activates the material and prevents the electrolyte degradations. During cycling, the derivative curves indicate at least 2 active redox couples [4]: $\text{Mn}^{3+}/\text{Mn}^{4+}$ (around 3.3V), $\text{Mn}^{4+}/\text{Mn}^{5+}$ and/or O^{2-}/O^- (around 4.1V). In order to have a better insight of lithium deinsertion process, we used magnetic measurements at various charge states. We will show that magnetic measurements are perfect tools to access to the oxidation level of the material, and in agreement with the values obtained after iodometric redox titrations. We will namely show that this material is oxidized up to Mn^{5+} oxidation state with a competition of the oxygen oxidation [4].

In short, in this work are reported the first results of a new electrochemically active compound as positive electrode for Li-ion batteries, with the active participation of both redox centers: Manganese and Oxygen [5].

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