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TEM and Raman spectroscopy evidence of layered to spinel phase transformation in layered $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ upon cycling to higher voltages

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ABSTRACT

Layered $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ was synthesized by a self-combustion reaction, characterized by XRD, SEM, TEM and Raman spectra, and was studied as a cathode material for Li-ion batteries. The electrochemical performance of this cathode material was tested in coin cells using galvanostatic charge–discharge cycling and electrochemical impedance spectroscopy (EIS). The galvanostatic cycling was performed in different potential ranges beginning with lower potential limit of 2.5 V and upper potentials of 4.2 V, 4.3 V and 4.6 V. Specific capacity values of 150 and 160 mA h g^{-1} are obtained when it is cycled between 2.5–4.2 V and 2.5–4.3 V, respectively. A higher specific capacity of about 190 mA h g^{-1} is obtained when cycled to the upper potential of 4.6 V. However, capacity fading and a shift of the average discharge voltage to lower values upon cycling was found when the electrodes were cycled in the range 2.5–4.6 V. The formation of a spinel-like phase was clearly identified from analysis by HRTEM and Raman spectroscopy of cycled electrodes when the upper potential limit was 4.6 V. These studies suggest that structural changes occur at potentials around 4.3 V that may affect the average potentials. EIS study indicates that there is an increase in the charge-transfer resistance at potentials higher than 4.4 V, suggesting that these electrodes develop low electronic conductivity, at least at the interfaces, when delithiated at high potentials.

1. Introduction

Li-ion batteries lead the market in powering portable electronic devices. The forecast for their production and consumption in the next year predicts an impressive increase. Li-ion batteries are being developed and implemented in more challenging applications such as electric vehicles and load-levelling. Their main advantages are their high energy density, good cyclability and reasonable rate capability [1–5]. $LiCoO_2$ is currently the main cathode material used in Li-ion batteries for portable electronic equipment. However, while this material is already a commercial widely used cathode material the use of this cathode material still raises some concerns about the cost, abundance of cobalt, and potential safety limitations at elevated temperatures [6]. Layered $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ is a promising cathode material from all points of view. Its Co content is only 1/3 of that of $LiCoO_2$, it exhibits impressive stability upon cycling, reasonable specific capacity (>150 mA h g^{-1}), good high rate capability, and good safety features [7–28]. It is iso-structural to layered $LiCoO_2$ and in fact seems to integrate the features of $LiCoO_2$, $LiNiO_2$ and $LiMnO_2$.

The electrochemical performance of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ depends on the particle size, crystallinity, surface morphology, porosity and potential range of cycling [16–24]. Martha et al. compared the electrochemical performance of nano and submicron $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ and found that nano-particles are not suitable for use due to their high surface reactivity (electrodes comprising nano-particles of this cathode material develop therefore too high impedance) [16]. Sinha et al. showed that porous $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, exhibited better electrochemical performance than non-porous $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ [18]. $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ can deliver a discharge capacity of 160 mA h g^{-1} via the Ni^{2+}/Ni^{4+} red-ox reaction when cycled up to a voltage of 4.3 V. This capacity is greater than that obtained from $LiCoO_2$. Even higher specific capacity can be obtained when cycled to higher voltages of 4.5 or 4.6 V, which enable use of the Co^{3+}/Co^{4+} redox reaction. Recently, there is an

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increasing interest on high capacity Li- and Mn-rich integrated cathode materials which have an initial structure containing the inactive component Li_2MnO_3 and the active component $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$. Polarization of this material to potentials higher than 4.6 V leads to a pronounced structural change, activation of the Li_2MnO_3 component and very high specific capacity (>250 mA h g^{-1}); capacity which tends to be retained even during prolonged cycling [29–39]. However, these materials exhibit structural changes upon cycling (there is evidence of partial transformation to spinel) what are expressed by a continuous decrease in the average discharge voltage, especially in the lower range of their voltage profile (<3.3 V). Due to their excellent properties and importance, $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ electrodes are being extensively explored. Many hundreds of papers have been published on this cathode material, including reporting on different synthesis routes and their effects on performance and on structural and electrochemical aspects behavior. Despite the enormous work invested so far in this cathode material, the complex interactions between the three transition metal ions, namely, Mn^{4+}, Ni^{2+} and Co^{3+} within the oxygen framework of layered $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ are not clearly understood. Also, the electrochemical stability of this material can vary depending on the voltage range in which it is operated. Here, we present a systematic study of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ electrodes upon cycling within 3 potential domains: 2.5–4.2 V, 2.5–4.3 V and 2.5–4.6 V. We intended to examine carefully the effect of the upper potential limit on the electrochemical properties (capacity, rates, stability and average voltage upon cycling), impedance and structure. We used self-combustion reaction for the synthesis in which the proper element mixing and the formation of oxides with the right stoichiometry is achieved by reacting metal nitrate precursors (at the appropriate ratios) with sucrose (which serves as a fuel), followed by calcination (in air) at high temperature). It is possible to achieve desirable particle size and morphology by the choice of temperature and the duration of the calcination. The characterization tools used in this study included standard electrochemical techniques, impedance spectroscopy, high resolution tunneling electron microscopy (HRTEM) and Raman spectroscopy.

2. Experimental

Analytical grade chemicals: $Mn(NO_3)_2$ (Fluka), $Co(NO_3)_2$, $Ni(NO_3)_2$, $LiNO_3$, sucrose, Poly(vinylidene fluoride) (PVDF), 1-methyl-2-pyrrolidinone (NMP) (Aldrich) were used as received. Double-distilled (DD) water was used to prepare the solutions of the metal nitrates and sucrose.

2.1. Synthesis and characterization of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

Layered cathode material $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ was synthesized by a self-combustion reaction using as precursors lithium, nickel, manganese and cobalt nitrates (acting as oxidants) and sucrose as the fuel, as reported earlier [17,18]. In a typical synthesis, 2.908 g of $Ni(NO_3)_2$, 2.910 g of $Co(NO_3)_2$, 2.510 g of $Mn(NO_3)_2$ and 2.170 g of $LiNO_3$ (Co:Ni:Mn:Li = 1:1:1:3) were dissolved in 60 ml of DD water. Then, sucrose (at a ratio of 1:2, metal nitrates to sucrose) was added to this solution with continuous stirring. The water was evaporated slowly by heating this mixture to produce a syrupy mass, which on further heating at 300 °C led to the self-ignition of the reactants to give the amorphous compound. The material was ground to a fine powder and annealed at 450 °C for 2 h in air. The product was ground a second time to form a fine powder that was then annealed in two steps: at 700 °C for 1 h and then at 900 °C for 22 h in air, resulting in well-crystallized $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ particles of sub-micron size, agglomerated to micron size clusters.

The structure of this material was characterized by X-ray diffraction with a Bruker D8 Advance X-ray diffractometer using Cu Kα (λ = 1.5418 Å) as the source. The morphology of the product was investigated with a scanning electron microscope Magellan XHR 400L FE-SEM-FEI. TEM structural characterization of this cathode material was carried out with a JEOL-JEM 2100 electron microscope with a LaB_6 emitter operating at 200 kV. Samples for the transmission electron microscope (TEM) studies were prepared by dispersing and sonicating the powdered samples in ethanol and adding a few drops of the resulting suspension to a TEM copper grid. These studies were performed in TEM mode using bright field imaging (BF), dark field (DF) imaging, conventional selected area electron diffraction (SAED) using a 300 nm aperture and nano-beam diffraction (NBD) using a 4 nm probe. In the DF mode, only specific sets of reflections (certain diffracted beams caused by a specific crystalline element) make up the image, hence the diffracting areas appear as bright spots in the DF image. In each case the DF images are taken using reflections unique to a chosen compound, hence a DF image displays the spatial distribution of that crystalline compound in the image. The structure assignment of the studied particles is based on analyzing the SAED and the NBD patterns data. The information imbedded in the reflections in these diffraction patterns allows us, in most cases, to establish unambiguously the exact structure of the compound. However, when there is structural similarity between different compounds, the same set of reflections may fit two or more compounds. Hence in such cases, the diffraction patterns alone cannot serve as conclusive evidence for structural determination. Micro-Raman spectroscopy studies of pristine and cycled electrodes were performed using a micro-Raman spectrometer from Renishaw inVia (UK) equipped with a 514 nm laser, a CCD camera, and an optical Leica microscope. A 50× objective lens to focus the incident beam and an 1800 lines/mm grating were used. We recorded spectra from 5 to 10 locations on each sample.

2.2. Electrode preparation

The electrodes for electrochemical studies were prepared by making a slurry of 80 wt% active material of $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$, 10 wt% of conductive super P carbon, and 10 wt% of PVDF binder in N-methyl-2-pyrrolidinone (NMP) as the solvent. The slurry was uniformly coated onto Al foil current collectors using a doctor-blade, dried at 80 °C for 12 h in an oven. The coated Al foil was then calendared uniformly and then cut into circular electrodes of 14 mm diameter. The electrodes were finally dried at 110 °C for 12 h under vacuum.

2.3. Electrochemical measurements

$LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ electrodes were tested using coin-type cells 2032 (NRC, Canada) assembled in an argon-filled dry glove box (made by MBroun or VAC). Li metal foil was used as the counter and reference electrodes. Typical loading of the active mass was 5–6 mg cm^{-2}. A commercial battery electrolyte solution LP 30 (Merck) consisting of 1 M $LiPF_6$ in ethylene carbonate/dimethyl carbonate (EC/DMC) (1:1 w/w) was used. A porous polypropylene-based membrane (Celgard) was used as the separator. The cells were stored for 12 h at room temperature after assembling, at OCV, in order to ensure the complete impregnation of the electrodes and the separators with the electrolyte solution. The cells