Variations in structure and electrochemistry of iron- and titanium-doped lithium nickel manganese oxyfluoride spinels

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HIGHLIGHTS

- The cycling of 2 Li eq. in doped $LiNi_{0.5}Mn_{1.5}O_4$/Li cells is analyzed.
- Postdoping with fluorine is leading to increased stability during cycling.
- An additional redox couple is found in the 4–4.5 V region.

ARTICLE INFO

ABSTRACT

Doping of cathode materials can considerably improve electrochemical performance and stability. Here, the high-voltage $LiNi_{0.5}Mn_{1.5}O_4$ spinel is used as a candidate material. It is high-voltage cycling at a potential of approximately 4.7 V and the ability to host 2 eq. Li, thus leading to a theoretical capacity of 294 mAh g^{-1}, that makes this material interesting. In order to improve stability and electronic conductivity, the spinel is doped with titanium and iron.

Cycling in a voltage range of 2.0–5.0 V leads to a cooperative Jahn-Teller distortion accompanied by a phase transformation from cubic to tetragonal symmetry. This causes a severe capacity fade. To improve capacity retention, the as-prepared spinel is post-doped with fluorine. Influence of different fluorine amounts in $LiNi_{0.5}Mn_{1.4}Fe_{0.1}Ti_{0.027}O_{4-x}F_x$ (x = 0–0.3) on the capacity and stability is analyzed. The initial capacities decrease with increasing fluorine content but the low voltage capacity is stabilized. Best electrochemical results are obtained with a fluorine content of x = 0.15. Furthermore, an additional redox couple is found. The intensity of this depends on the fluorine content. It is assumed that manganese, either in the tetrahedral sites or in octahedral sites, bound to fluorine lead to a higher voltage.

1. Introduction

Current research into cathode materials mainly focuses on the development of high-capacity materials (e.g. Li-rich layered oxides [1–3]) and high-voltage materials (e.g. $LiNi_{0.5}Mn_{1.5}O_4$ [4,5]). The common goal of both research directions is to achieve a higher specific energy or energy density. While materials with high capacities exhibit relatively low mean voltages around 3.5 V vs Li^+/Li, high-voltage materials, such as $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) spinel, suffer from poor capacities of ~147 mAh g^{-1} and low cycling stability when cycled vs. graphitic anode materials [6–8]. Stable cycling of LNMO at high voltages can be achieved when lithium metal is used as anode material [9–11].

In addition to stable cycling, use of lithium metal allows for cycling 2 eq. of lithium per cycle, since the LNMO structure can accommodate additional lithium in the 16c octahedral sites [12,13]. Thus, theoretical capacity of LNMO increases up to 294 mAh $^{-1}$, leading to a theoretical energy of around ~1100 Wh kg^{-1} in comparison to ~900 Wh kg^{-1} for NMC materials [14].

Using the whole voltage range of 2.0–5.0 V vs. Li^+/Li, however, is associated with a phase transition from cubic to tetragonal symmetry due to a cooperative Jahn-Teller-distortion [12,15,16]. This process leads to a severe capacity fade which limits the use of this extended voltage range for the LNMO\\Li metal system.

Several studies revealed that doping LNMO with various elements can have a huge impact on electrochemistry as well as on stability (e.g. Cr, Fe, Ga [17]; Fe, Cu, Al, Mg [18]; Ti [19]). It was also shown for the $LiMn_2O_4$ spinel that anion doping in addition to cation doping can improve cycling stability and helps to mitigate the cooperative Jahn-Teller distortion [20].

In this study, titanium and iron are used to increase the lattice parameter of the spinel in order to enhance stability [11,19] and to increase the electronic conductivity [21]. The iron- and titanium-doped spinel is post-doped with various amounts of fluorine which can enhance the stability during discharging to 2.0 V [22].

Although several studies have been published on iron- and/or titanium-doped LNMO spinels [11,17–19,23–25] as well as on fluorine-doped LNMO spinels [26–30] and on the cycling of $LiMn_2O_4$ and its derivatives in a voltage range of 2.0–5.0 V vs. Li^+/Li [12,13,20,31], studies addressing the changes of structure and electrochemistry for iron- and titanium-doped lithium nickel manganese oxyfluoride spinels as a function of the fluorine content in the large voltage range are still lacking.

For this reason, the chemical and structural compositions of the as-synthesized samples are analyzed as a function of the different fluorine amounts by means of inductively coupled emission spectroscopy (ICP-OES), scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) as well as by ^7Li magic-angle spinning (MAS) NMR spectroscopy. Furthermore, the effects of fluorine on the electrochemical behavior in the voltage range from 2.0 to 5.0 V vs. Li^+/Li are discussed.

2. Experimental section

2.1. Synthesis

To obtain the iron- and titanium-doped spinel, a two-step synthesis was used. This process is based on a modified version of the process described by Schroeder et al. [11]. Metal acetates of lithium, nickel, and manganese ($Li(OOCCH_3)\cdot2H_2O$, Alfa Aesar; $Ni(OOCCH_3)_2\cdot4H_2O$, and $Mn(OOCCH_3)_2\cdot4H_2O$, Sigma Aldrich) as well as iron nitrate ($Fe(NO_3)_3\cdot9H_2O$, Alfa Aesar) are used as precursor materials to synthesize the iron-doped $LiNi_{05}Mn_{1.5}O_4$ by spray drying (Mobile Minor 2000, Niro A/S) of an aqueous solution. The amount of iron is adjusted to yield a spinel composition of $LiNi_{0.5}Mn_{1.4}Fe_{0.1}O_4$. The powder is calcined at 800 °C for 10 h.

Titanium doping is achieved in a post-treatment with a titanium-containing sol. For this, the spinel powder is ground with a planetary ball mill (Pulverisette 5, Fritsch) for 24 h using yttria-stabilized zirconia beads. After 23 h, a sol consisting of lithium acetate (Alfa Aesar), titanium isopropoxide ($Ti[OCH(CH_3)_2]_4$, Merck), and acetic acid (Li:Ti:acetic acid = 1.33:1.67:1.67) in water is added to the dispersion. The amount of the sol was adjusted to 1.67 mol%. The dispersion was spray-dried again and a final calcination step at 780 °C for 10 h leads to the Fe, Ti-doped LNMO spinel. The desired composition of $LiNi_{0.5}Mn_{1.4}Fe_{0.1}Ti_{0.027}O_4$ was chosen based on previous studies, in which it exhibited good cycling properties [11,22]. The as-prepared iron- and titanium-doped LNMO is used as a reference and starting material for the fluorination process.

In order to maintain the as-prepared morphology and to ensure that the starting material has the same composition for different fluorinated samples, a post-doping process is applied. Fluorination takes place by a gas-solid reaction at elevated temperatures. For this, the as-prepared spinel powder is placed in a small open Ni crucible which is placed in a closed larger Ni crucible. The larger crucible contains a powder bed consisting of CoF_3 (Sigma Aldrich), which is used as a fluorination agent. During thermal treatment, decomposition of CoF_3 occurs and a fluorine atmosphere is generated [32]. The heating rate is 5 K/min up to the desired annealing temperatures (600 °C, 700 °C, and 750 °C). The temperatures are maintained for 10 h and the cooling rate is 5 K/min. Due to the different temperatures, different amounts of fluorine are released from CoF_3, the extent of fluorine doping is increased with the annealing temperature.

For simplification, the different synthesized materials are abbreviated as LNMO-noF (reference spinel), LNMO-F600, LNMO-F700, and LNMO-F750 fluorinated at 600 °C, 700 °C, and 750 °C, respectively.

In addition to the fluorinated samples, two reference samples are prepared. These reference samples are prepared similar to the LNMO-F700 and LNMO-F750 samples. However, annealing was performed without a fluorine-containing powder bed. The purpose of these blank samples is to identify whether observed changes in structure and electrochemical behavior are due to fluorine doping or oxygen loss. Oxygen loss in LNMO spinels occurs at temperatures above 700 °C [33]. The blank samples are denoted LNMO-noF700 and LNMO-noF750 for annealing temperatures of 700 and 750 °C, respectively.

2.2. Chemical and structural characterization

Different analytical methods were applied to obtain information about the chemical and physical composition of the synthesized materials. A field emission scanning electron microscope (Supra 55, Zeiss) was used to analyze morphological features of the material. Micrographs were obtained with an accelerating voltage of 10 kV.

The specific surface area (A_{BET}) was analyzed using nitrogen physical adsorption isotherms measured with a Gemini VII 2390 (Micromeritics GmbH). Calculation was performed according to the BET theory [34].

Chemical analysis was done using inductively coupled emission spectroscopy (ICP-OES). The measurements were performed with the help of an OPTIMA 4300DV spectrometer (Perkin-Elmer). The spectrometer was equipped with Echelle optics and a segmented diode array. Prior to the measurements, the samples were dissolved in nitric acid/hydrochloric acid. All samples were analyzed three times in order to determine the concentrations of lithium, nickel, manganese, iron, titanium, and cobalt. The fluorine content in the bulk sample was analyzed using an ion selective electrode.

X-ray diffraction patterns were collected by means of a D5005 diffractometer (Siemens). Cu $K\alpha$ radiation and a Sol-X detector was used for measurements. A range from 15° to 80° 2Θ was covered with steps of 0.04° and a counting time of 12 s.

For additional structural characterization of the synthesized spinel powders, Fourier transform infrared spectroscopy (FTIR, Vertex 70 Bruker) was applied. Spectra were obtained as an average of 15 scans of a very small amount of powder in KBr.

^7Li magic-angle spinning (MAS) NMR spectroscopy was performed at room temperature with a Bruker Avance 200 MHz spectrometer at a magnetic field of 4.7 T corresponding to a Larmor frequency of L = 77.8 MHz. A spinning speed of 30 kHz was applied using 2.5 mm rotors. A 1 M LiCl solution served as ^7Li reference (0 ppm). The typical value for the recycling delay of ^7Li was 1 s. ^7Li MAS NMR experiments were run with a rotor-synchronized Hahn-echo sequence ($\pi/2-\tau-\pi-\tau-$acquisition) and a typical $\pi/2$ pulse length of 2 μs.

2.3. Electrochemical characterization

Cathode films were prepared by blade coating of the slurry on an aluminum foil current collector. The slurry consisted of the spinel powder, carbon black (C-Nergy Super C65, Timcal), and PVDF