



Evidence of loss of active lithium in titanium-doped $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ /graphite cells



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HIGHLIGHTS

- We use three electrode $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ /graphite cells to study capacity fade.
- Capacity fade in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ /graphite cells occurs due to loss of active lithium.
- The high voltage spinel is not damaged during cycling.
- A mathematical model based on zero order reaction kinetics describes capacity fade.

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ABSTRACT

Lithium-ion batteries require higher energy densities to meet with a broad acceptance in the fields of electric vehicles and grid storage solutions. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) can fulfill this goal due to its high operating voltage. Cycling of LNMO is known to be stable vs. lithium metal anode. Cycling in an LNMO/graphite configuration leads to severe capacity fade. Ti-doped LNMO (LNMTO)/graphite cells experience a lower, but still strong loss of capacity. In order to understand capacity fade, cycling tests of LNMTO vs. graphite and vs. lithium metal were carried out and additionally, three electrode tests were performed. Both cell configurations showed similar Coulombic efficiencies correlating with the applied C-rate. Experimental data and mathematical modeling indicated that loss of active lithium with a constant reaction rate of $(3.76 \pm 0.46) \cdot 10^{-8} \text{ mol Li h}^{-1}$ is responsible for capacity fade in LNMTO/graphite cells and that no degradation of the active material occurs. It was concluded that lithium loss also occurs when lithium metal anodes are used. Here, the lithium metal anode can compensate for lithium consumption, as a result of which the capacity is not influenced. Further support for lithium consumption is given by a three-electrode cell with a lithiated graphite anode. The lithium in the graphite anode can compensate the lithium loss for 120 cycles. During this time, the cell experienced hardly any capacity fade and the voltage profile was similar to that of a cell with LNMTO/Li configuration.

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1. Introduction

High energy densities are mandatory to enhance the acceptance of lithium-ion batteries in the fields of electric vehicles and grid storage solutions. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) spinel offers a higher energy density than commercial cathode materials (e.g. LiFePO_4). This is due to the high operating voltage of $\sim 4.7 \text{ V}$ [1]. Cycling of LNMO vs. lithium metal is known to be very stable [2–5] and the theoretical capacity can be nearly reached. When cycling LNMO vs.

a graphite anode, severe capacity fade occurs [6–8]. Several phenomena leading to capacity fade of Li-ion batteries are described in literature (e.g. electrolyte oxidation, loss or degradation of active material, Mn^{2+} dissolution, and loss of lithium [8–12]). According to the study of Kim et al. [8], the main reason of capacity fade of high-voltage spinel vs. graphite is the loss of electrochemically active lithium and not the degradation of the active material. A drawback of their study is the experimental setting. To separate anode and cathode effects, they compare profiles of LNMO/graphite cells with calculated profiles of LNMO/Li and graphite/Li cells. Consequently, the processes on the anode and on the cathode side of an LNMO/graphite cell can only be observed indirectly.

In an earlier study, we showed that doping of the LNMO with titanium (LNMTO) leads to a better cycling stability as well as rate performance [4]. Furthermore, the capacity retention of LNMTO/

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graphite cells is increased compared to LNMTO/graphite cells [13,14]. Here, we use the titanium-doped spinel to test the hypothesis of lithium loss. Testing of LNMTO vs. graphite and vs. a lithium metal anode and subsequent use of three-electrode cells allow to identify a possible loss of lithium. A combination of the experimental results and a simple mathematical model is used for a better understanding of capacity loss with the cycle number and time. When using three-electrode cells, it is possible to distinguish electrochemical processes on the cathode as well as on the anode side, while the cell is cycled in LNMTO/graphite configuration. Results show that the active material is not damaged and that lithium loss can be calculated using a constant reaction rate.

2. Experimental section

2.1. Synthesis

The Ti-doped $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMTO) was obtained by a two-step method described in detail by Schroeder et al. [4]. In a first step the LNMO was synthesized by spray drying (Mobile Minor 2000, Niro A/S) of an aqueous solution of the corresponding metal acetates ($\text{Li}(\text{OOCCH}_3) \cdot 2\text{H}_2\text{O}$, Alfa Aesar; $\text{Ni}(\text{OOCCH}_3)_2 \cdot 4\text{H}_2\text{O}$, and $\text{Mn}(\text{OOCCH}_3)_2 \cdot 4\text{H}_2\text{O}$, Sigma Aldrich), followed by calcination under air at 800°C for 2 h. The obtained spinel was ground for 24 h with ethanol in a planetary ball mill (Pulverisette 5, Fritsch) using yttria-stabilized zirconia beads. A sol consisting of lithium acetate (Alfa Aesar), tetra-*n*-butyl orthotitanate (Merck), and acetic acid ($\text{Li}:\text{Ti}:\text{acetic acid} = 1.33:1.67:1.67$) in ethanol was added to the dispersion. The amount of the sol was adjusted to 1.67 mol%. Repeated spray drying followed by calcination at 780°C for 2 h led to the final LNMTO powder.

2.2. Chemical and structural characterization

The elemental composition of the LNMTO powder was determined by inductively coupled emission spectroscopy (ICP-OES). Measurements were performed using an OPTIMA 4399DV 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, titanium, manganese, and nickel.

Mercury intrusion porosimetry was performed for analyzing the porosity (CEI Pascal 1.05, Thermo Electron). The relative porosity ($P = V_p/[V_p + 1/\rho]$) was calculated using the measured specific pore volume (V_p) for pore widths <600 nm and the density calculated from the Rietveld refinement of the X-ray diffractogram ($\rho = 4.44 \text{ g cm}^{-3}$).

In order to determine the specific surface area (A_{BET}), nitrogen physical adsorption isotherms were measured (Gemini VII 2390, Micromeritics GmbH). The calculation of A_{BET} was performed according to the BET theory [15]. The specific surface area was used to calculate the mean equivalent grain diameter ($d_{\text{BET}} = 6/(\rho \cdot A_{\text{BET}}) \cdot 10^{-6}$ in m).

A field emission scanning electron microscope (Supra 55, Zeiss) was used with an accelerating voltage of 10 kV for observation of particle surfaces. Cross sections of the cathode films were prepared with an ion beam slope cutter (Leica EM TIC 3X, Leica Microsystems) with a triple ion beam.

XRD patterns were collected with a D5005 diffractometer made by Siemens. The diffractometer was equipped with a Cu-K_α source and a Sol-X detector. Measurements were performed between 15 and $80^\circ 2\theta$ with steps of 0.04° and a dwell time of 4 s. Rietveld refinement was done using the TOPAS 4.2 software (Bruker AXS).

2.3. Electrochemical characterization

For the preparation of the cathode film, a homogeneous slurry consisting of the LNMTO powder, carbon black (C-Nergy Super C65, Timcal), and PVDF binder (Solef PVDF 5130/1001, Solvay) using a weight to weight ratio of 85:10:5 dispersed in *N*-methyl-2-pyrrolidone (NMP, Merck) was produced. The slurry was cast onto an aluminum foil current collector using a continuous coating system (KTF-S, Mathis) and dried at 80°C for 24 h. The resultant LNMTO cathode film had an active material loading of $6.5 \pm 0.2 \text{ mg cm}^{-2}$ and a porosity of $76.0 \pm 1.5\%$.

Electrochemical characterization was performed with two and three-electrode Swagelok-type cells assembled in an argon-filled glove box (<1 ppm H_2O). A glass fiber separator (GF/C, Whatman) and 120 μl electrolyte consisting of EC:DMC at a ratio of 1:1 and 1 M LiPF_6 (LP30, Merck) were used. Two electrode cells were equipped either with a lithium metal anode or with a graphite anode ($10.2 \pm 0.2 \text{ mg cm}^{-2}$ loading, resulting in a cathode/anode capacity ratio of 0.4). Three-electrode Swagelok cells use graphite anodes and lithium metal as a reference electrode.

The graphite anodes for use in the three electrode cells were subjected to different pretreatments. They were precycled against commercial NMC ($\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$) cathode material between 3.0 and 4.2 V for ten cycles. Precycling was to result in a stable solid electrolyte interface (SEI) on the surface of the anodes. Cycling of the NMC/graphite cells was stopped at two different state of charge (SOC), one at ~50% SOC (3.7 V) and one at 0% SOC (3.0 V). Thus, the anode of the cell at 50% SOC contained intercalated lithium, while the cell with 0% SOC contained no cyclable lithium. Afterwards, the C/NMC cells were dismantled in an argon-filled glove box. The anodes were washed with DMC and incorporated in new three-electrode cells together with fresh electrolyte, LNMTO cathodes, and lithium metal reference electrodes. The cells were then referred to as LNMTO/ $C_{\text{D}}(\text{elithiated})$ and LNMTO/ $C_{\text{L}}(\text{ithiated})$ for the NMC/graphite cells stopped at 3.0 V and 3.7 V, respectively. A third three-electrode cell with a fresh anode (LNMTO/ $C_{\text{F}}(\text{resh})$) was prepared for comparison.

Galvanostatic cycling tests were performed using a BT2000 battery cycler (Arbin Instruments). Cells were cycled in a voltage range between 3.5 and 5.0 V with two cycles at $C/20$ (7.3 mA g^{-1}) at the beginning, if not otherwise indicated. In all cycling tests, the internal cell resistance (IR) was determined every 10th cycle at 4.7 V (SOC ~50%) using a built-in function of the Arbin test device [16]. Current pulses (amplitude $\Delta I = \pm 0.1 \text{ mA}$, length $t = 80 \text{ ms}$) are applied 10 times on top of the discharge current I_0 . The internal resistance is calculated by $IR = \sum_{i=1}^{10} [U(I_0 + \Delta I) - U(I_0 - \Delta I)] / [20 \Delta I]$.

3. Results and discussion

3.1. Powder and cathode film properties

The composition of the synthesized powder was analyzed by XRD and ICP-OES. The elemental composition given in Table 1 is in good agreement with the theoretically expected stoichiometry $\text{Li}_{1.006}\text{Ni}_{0.492}\text{Mn}_{1.475}\text{Ti}_{0.028}\text{O}_4$. Fig. 1 shows the XRD pattern and the Rietveld refinement. Calculation of the pattern is based on a disordered LNMO spinel with a space group of $Fd\bar{3}m$. The cubic lattice parameter is calculated to be $8.1737(1) \text{ \AA}$, which is in good agreement with earlier results of $8.1747(2) \text{ \AA}$ [4]. $\text{Li}_x\text{Ni}_{1-x}\text{O}$, a well-known impurity phase [1,17], is found with a minor amount of <2 wt%.

SEM micrographs (Fig. 2) show that the LNMTO powder consists of spherical granules of $8 \pm 3 \mu\text{m}$ in diameter. The primary particles are in the range of tens to a few hundred nanometers with a few

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