



Delithiation/relithiation process of LiCoMnO₄ spinel as 5 V electrode material



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HIGHLIGHTS

- LiCoMnO₄ has been synthesized via sol-gel route.
- LiCoMnO₄ provides electrochemical performance above 5 V over 100 cycles.
- Lithiation-/delithiation process has been revealed via *in situ* diffraction.
- Complete delithiation of LiCoMnO₄ is reached at 5.6 V.
- Co³⁺ and Mn⁴⁺ are distributed homogeneously throughout the material.

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ABSTRACT

In this work, the LiCoMnO₄ spinel has been synthesized by a two-step sol-gel based method, followed by sintering at temperatures up to 750 °C in oxygen. After structural characterization of the pristine material via synchrotron and neutron diffraction, the material was characterized via SEM and ⁶Li-MAS-NMR spectroscopy. ⁶Li-MAS-NMR spectroscopy in different states of charge revealed, that manganese and cobalt are distributed homogeneously throughout the material and the delithiation primary occurs from the manganese environments. It was also shown, that it is not possible to fully delithiate the material in a practical voltage range of an electrolyte. Electrochemical cycling results reveal that about 70% of the lithium can be extracted and reinserted electrochemically in the voltage window from 4.5 to 5.4 V against lithium from/into LiCoMnO₄. *In situ* synchrotron powder diffraction results show that lithium extraction/insertion occurs via a single-phase mechanism over the whole range of lithium contents and that the discharge capacity is mainly restricted by the voltage-window of the electrolyte. Furthermore it was shown, that the delithiation occurs up to a potential of 5.6 V.

1. Introduction

Although lithium-ion batteries (LIB) are already used as energy storage systems in a huge variety of devices and applications, their energy density, rate capability, cycle life and cost efficiency have to be further improved [1] for future applications. A well-known material for LIBs is the lithium manganese spinel LiMn₂O₄, which is nontoxic and cheaper than the established LiCoO₂, but suffers from a lower specific capacity and a fast capacity fading [2]. This capacity fading is mostly attributed to Mn³⁺ in the structure, which on the one hand can lead to dissolution of manganese due to disproportionation to Mn⁴⁺ and to the

dissoluble Mn²⁺. On the other hand, Mn³⁺ exhibits Jahn-Teller distortion, which also leads to degradation in the host lattice, especially if it is oxidized to Mn⁴⁺ during charging and reduced back to Mn³⁺ during discharging of the cell [3,4]. To overcome some or all of these problems, it is necessary to reduce the amount of Mn³⁺ in the structure. This can be done by substituting manganese in the general formula LiM_xMn_{2-x}O₄ with other metal ions M like Co³⁺, Cr³⁺, Ni²⁺, Fe³⁺ or Ti⁴⁺ [5]. This can also increase the energy density of the spinel system by raising the operating voltage of the cell in comparison to pure LiMn₂O₄, i.e. from values around 4 V to values up to 5 V [5–7].

In this study, we focus on LiM_xMn_{2-x}O₄, where M¹ is Co³⁺ and x is

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equal to 1. This material was first investigated as active material for lithium ion batteries in 1999 from Kawai et al. [7], but suffers from a high degradation during cycling, as well as a relatively low discharge capacity [6,8–11]. The reasons for the low cycle life and discharge capacity are still unknown. In principle, there are at least three possibilities to explain the low discharge capacity: (1) it is not possible to delithiate the material up to 100% in the used voltage range and the achieved charge capacity also contains contribution from parasitic side reactions with the electrolyte or (2) the complete charging leads to irreversible changes in the structure and parts of the contained lithium ions cannot take part in the de-/intercalation process or (3) the investigated samples are not phase pure and an considerable amount of lithium is "trapped" in an inactive phase. To further study these issues, *in situ* synchrotron diffraction experiments, as well as *ex situ* ^6Li NMR and magnetization experiments were conducted.

2. Experimental

In order to synthesize LiCoMnO_4 , a adapted Pechini based sol-gel route has been used [12]. Citric acid and ethylene glycol (1:4 mol eq.) have been mixed at 50 °C, then the metal acetates have been added to the solution ($\text{LiCH}_3\text{COO}\cdot 2\text{H}_2\text{O}$, $\text{Mn}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$, all Sigma Aldrich, reagent grade). The resulting solution was then stirred for 12 h at 90 °C. After stirring, the excess of ethylene glycol and water residues were evaporated at 180 °C, leading to a violet gel, which was pre-calcined at 350 °C for 3 h in a muffle furnace (Nabertherm L5/12) under air atmosphere to obtain the precursor powder. The precursor powder was ground in a mortar and again calcined in a tube furnace (Carbolite CTF 18/300) under oxygen atmosphere (2 L min^{-1}) for 24 h at 600 °C, directly followed by 12 h at 750 °C, also under oxygen atmosphere, with a heating and cooling rate of $3\text{ }^\circ\text{C min}^{-1}$. In contrast to other spinel systems like $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, a calcination temperature of 1000 °C leads to a more pronounced irreversible oxygen loss, which cannot be completely annealed [11,13].

For ^6Li magic-angle spinning (MAS) NMR, a Bruker Avance 200 MHz spectrometer (4.7 T) with 1.3 mm zirconia rotors and a spinning frequency of 67 kHz was used. The experiments were performed with a rotor synchronized Hahn-echo pulse sequence ($\pi/2$ - τ - π - τ -acquisition), a $\pi/2$ pulse length of 0.95 μs and a recycle delay of 0.1 s. All spectra were acquired at 283 K with 700,000 scans and a typical sample mass of 5 mg. An aqueous 1 M LiCl solution was used as the reference for the chemical shift of ^6Li (0 ppm).

The morphology of the particles was analyzed with a Zeiss MERLIN SEM (Scanning Electron Microscope) with a primary electron energy of 10 keV and an in-lens detector.

To obtain cathodes for electrochemical characterizations, pristine LiCoMnO_4 powder (80 wt.-%) has been ground with carbon black (10 wt.-%, TIMCAL, Super C65) and PVDF (10 wt.-%, Solef 6020, Solvay) and NMP (Sigma-Aldrich) resulting in a slurry, which was then coated on aluminum foil (20 μm) with a wet thickness of 180 μm . This film was then dried at 80 °C for 24 h and discs were punched out with a diameter of 14 mm. The mass loadings of the electrodes were $\sim 5\text{ mg}$ composite. Coin cells were assembled in an argon filled glove box (MBraun) with lithium foil (MTI, 15.6 mm diameter, 250 μm thickness) as anode, 180 μL electrolyte and two layers of Celgard 2325 as separator. All cells were cycled with a VMP3 multi-channel potentiostat (Bio-Logic, France) at 25 °C. The electrolyte used for cells cycled in the voltage range of 5.3–4.5 V was LP30 (1 M LiPF_6 in EC:DMC (50:50, wt.), BASF). Since LP30 is not stable above 5.3 V, another electrolyte was used (CDF6) for tests above 5.3 V, containing 1 M LiPF_6 (ABCR) and a 50:50 (wt.) mixture of Bis(2,2,2-Trifluoroethyl) Carbonate and 4-Fluoro-1,3-dioxolan-2-one (TCL). The neutron powder diffraction experiments were performed at the high-resolution powder diffractometer SPODI [14] at ambient temperature using monochromatic neutrons with $\lambda = 1.54757(7)\text{ \AA}$. Its vertically position-sensitive multidetector consists of 80 ^3He tubes with an effective height of 300 mm and covers

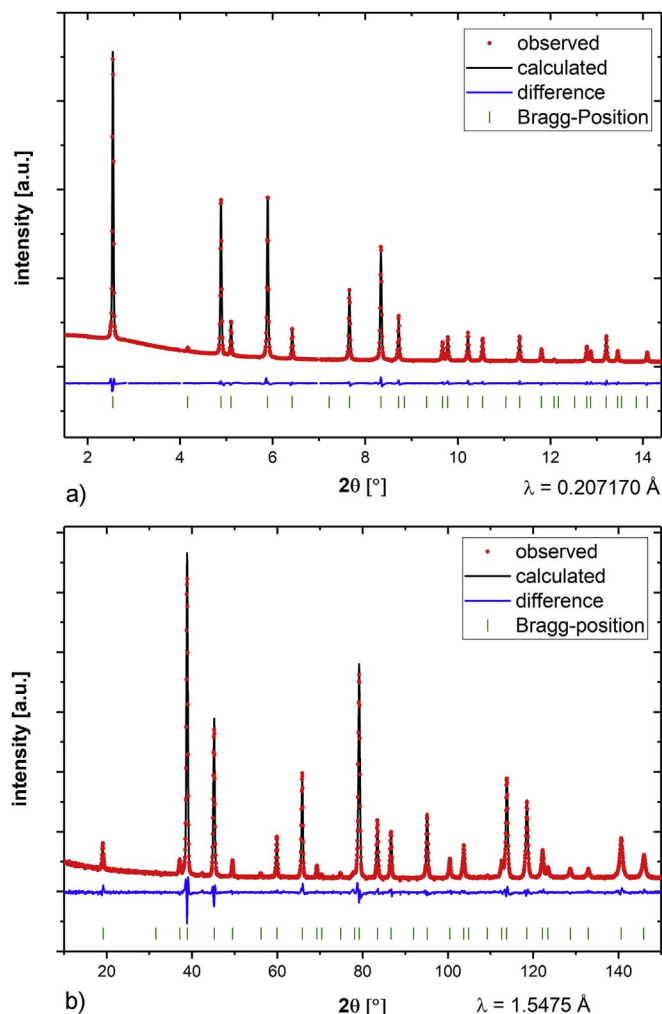


Fig. 1. Simultaneous Rietveld refinement against synchrotron diffraction a) and neutron diffraction b) data of LiCoMnO_4 .

Table 1

Neutron and Synchrotron diffraction Rietveld corefinement results for LiCoMnO_4 . $a = 8.05299(2)$, SG $\text{Fd}\bar{3}m$, origin choice 2. Berar & Lelann [20] corrected estimated standard deviations are given in parentheses.

Atom	x	y	z	Occupancy
Li_{8a}	1/8	1/8	1/8	0.943(7)
Co_{8a}	1/8	1/8	1/8	0.057(7)
Co_{16d}	1/2	1/2	1/2	0.472(4)
Mn_{16d}	1/2	1/2	1/2	0.5
Li_{16d}	1/2	1/2	1/2	0.024(4)
O_{32c}	0.26290(6)	0.26290(6)	0.26290(6)	1

an angular range of 2θ from 0° to 160°. All measurements were performed in Debye–Scherrer geometry with an incident neutron beam having a rectangular cross section at the sample position of $40 \times 30\text{ mm}^2$.

In situ synchrotron powder diffraction experiments were performed at the Materials Science and Powder Diffraction Beam Line (MSPD) at ALBA at 30 keV ($\lambda = 0.413426\text{ \AA}$), using a MYTHEN 6 K Position Sensitive Detector [15] and a dedicated coincell setup [16] with an exposure time of 45 s.

Ex situ synchrotron powder diffraction experiments were performed in 0.5 mm capillaries at the high resolution beamline (P02.1) at PETRA-III, DESY, at 60 keV ($\lambda = 0.20717\text{ \AA}$), with an exposure time of 60 s. The diffraction patterns were acquired using a 2D flat panel detector

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