Laser Micro Structuring of Composite $Li(Ni_{0.6}Mn_{0.2}Co_{0.2})O_2$ Cathode Layers for Lithium-Ion Batteries

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***Abstract*— Lithium-ion batteries (LIB) using lithium nickel manganese cobalt oxide ($Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$, NMC-111) as cathode material have already become one of the most important types of mobile power sources due to their high gravimetric and volumetric capacity. Nevertheless, the automotive industry needs batteries with a further improved energy density to develop electric vehicles (EV) with comparable or even higher range than automobiles with ICE (Internal combustion engine). One approach to enhance the energy density is to increase the nickel content of the NMC cathode material. Therefore, NMC-622 cathodes were produced via tape casting containing 80 wt% of active material with a film thickness of 54 µm. The specific capacities were measured using galvanostatic measurements at different charging/discharging currents for cells with structured and unstructured electrodes. Laser-assisted generation of three-dimensional architectures provides an increased active surface area to enhance interfacial kinetics with short lithium-ion diffusion paths. Ultrafast laser ablation was used in order to avoid a thermal-induced damage of the active material. It could be shown that laser structuring of electrode material leads to a significant improvement of the electrochemical performance, especially at high charging and discharging currents.**

Keywords*— *lithium-ion battery, lithium nickel manganese cobalt oxide, battery performance, laser structuring, ultrafast laser, 3D battery, nickel-rich NMC, high power battery

I. INTRODUCTION

The automobile industry intends to further move from conventional vehicles using internal combustion engine (ICE) towards hybrid electric vehicles (HEV) and electric vehicles (EV) [1,2]. One main aspect hereby is the usage of lithium-ion batteries (LIBs) due to their high gravimetric and volumetric capacity, low self-discharge and high cycle life-time as a mobile energy storage device [3-5]. In order to overcome the drawback of a decreased range of EV, a high energy density of about 250 Wh kg^{-1} on cell level in 2020 is desired [6]. However to meet this requirement, a high energy cathode material is needed. State-of-the-art cathode material in commercial lithium-ion batteries is lithium nickel manganese cobalt oxide $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ (NMC-111). NMC-111 provides many advantages such as high energy density (>150 Wh kg^{-1}) on cell level, high power density (650 W kg-1 @ 25 °C and 50 % Depth of Discharge) [7], high rate capability, high specific capacity (163 mAh/g), and good thermal stability in the fully charged state [8]. In 2013, Noh et al. [9] could show that the initial discharge capacities are higher for nickel-rich NMC in comparison to NMC-111. The nickel-enriched cathode material of $Li(Ni_xMn_yCo_z)O_2$ can provide discharge capacities up to 187 mAh/g for x=0.6 (NMC-622) and 203 mAh/g for x=0.8 (NMC-811), respectively.

In this work, we will apply the three-dimensional (3D) battery concept on NMC-622 cathode material. For this purpose, ultrafast laser-assisted will be applied in order to enhance interfacial kinetics. Besides an improved electrochemical performance, a reduction of battery manufacturing costs is expected [10-13].

II. EXPERIMENTAL

A. Tape-casting of processed nickel enriched NMC cathodes for lithium ion batteries

NMC thick film electrodes were produced via tape-casting. The slurry containing 80 wt% of NMC-622 (Targray, Canada), 10 wt% of conductive agent (TIMCAL SUPER C65, MTI Corporation, USA) and 10 wt% of polyvinylidene fluoride binder (PVDF, MTI Corporation, USA) was spread on a 20 µm thick aluminum substrate using a doctor blade on a film coater (MSK-AFA-III, MTI Corporation, USA). Afterwards the electrodes were dried at 50 °C temperature for 2h. In order to achieve a similar thickness and porosity the thick film cathodes were calendered using a hot rolling press (Precision 4" Hot Rolling Press/Calender, MTI Corporation, USA) at 50 °C temperature using a constant speed of 8 mm/s.

B. Laser micro structuring of thick film electrodes

The laser ablation process was carried out by an ultrafast fiber laser (Tangerine, Amplitude Systèmes, France) providing an average power of 35 W and a maximum pulse energy of 175 µJ at 1030 nm (TEM_{00} with $M^2 < 1.2$) working inside a highly flexible laser micromachining system (PS450-TO, Optec s.a., Belgium). The pulse duration is tunable from 380 fs up to 10 ps. Also second- and third harmonic generation (SHG and THG) is possible up to repetition rates of

2 MHz. The ablation process was carried out using a laser repetition rate of 200 kHz, a laser pulse duration of 380 fs, and a laser wavelength of 515 nm. Line structures were generated with a pitch distance of 200 µm (Figure 1). An average power of 2 W was applied, working with a F-Theta of 100 mm and a pre-positioned beam expander (3 x fold). The scanning velocity was set to 500 mm/s and 3 scanning repetitions were required. After the structuring process, the NMC cathodes were cut 12 mm in diameter electrodes using the same ultrafast laser system with an average power of 5 W, a scanning velocity of 300 mm/s and 7 scanning repetitions. For both, cutting and structuring process, an external exhaust next to the samples removed the ablated material while working at ambient air.

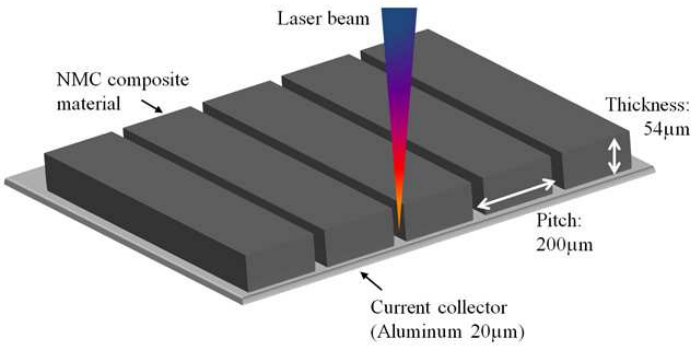

Figure 1: Schematic view of the laser structuring process of NMC thick film cathodes.

C. *Cell assembling and electrochemical characterization*

The cathodes were heated in a vacuum oven (VT 6025, Thermo SCIENTIFIC, Germany) for 24 h at 130°C for subsequent cell assembling in an argon-filled glove box (LABmaster sp, M. Braun Inertgas-Systeme GmbH, H_2O < 0.1 ppm and O_2 < 0.1 ppm) using Swagelok© design with 12 mm in diameter for the NMC cathodes and lithium metal (Sigma Aldrich Chemistry, USA) as counter electrode. The principle set-up of the electrochemical cell is described elsewhere [14]. The electrolyte consisted of ethylene carbonate (EC) and dimethyl carbonate (DMC) with 1 M lithium hexafluorophosphate LiPF6 (EC:DMC 1:1, 1M LiPF6, BASF, Germany) and a glass micro-fiber (GF/A filter, Whatman Company, UK) with a thickness of 260 µm was used as a separator. To avoid insufficient electrolyte wetting, the unstructured cathode material was stored in an electrolyte bath before cell assembling. Two hours after assembling, the electrochemical formation process took place in a battery cycler (BT2000, Arbin Instruments, USA). The cells were charged and discharged with a rate of C/10 (charging/discharging in 10 hours) for 5 cycles in a voltage range from 3.0 – 4.3 V. After this process, cyclic voltammetry (CV) measurements were performed using a sweep rate of 0.02 mV/s for 3 cycles. Further galvanostatic measurements were recorded with a constant charging rate of C/5 while changing the discharging rate from C/5 to C/2 for 5 cycles up to subsequently higher discharging rates of 1C, 2C, 3C, 5C, 7C and 10C, respectively using the same voltage window.

II. Results and Discussion

A. *Tape-casting and calendering process of nickel enriched NMC electrodes*

The produced thick films were measured before (79 µm thickness without current collector) and after (54 µm) the calendering process by using scanning electron microscopy and cross section analysis of the thick film layers as well as fluorescence microscopy, as shown in Figure 2a. The calendering process leads to a homogenous film thickness as well as to an adjustment of the porosity. It also improves the particle-to-particle contact. A schematic view of the process can be shown in Figure 2b.

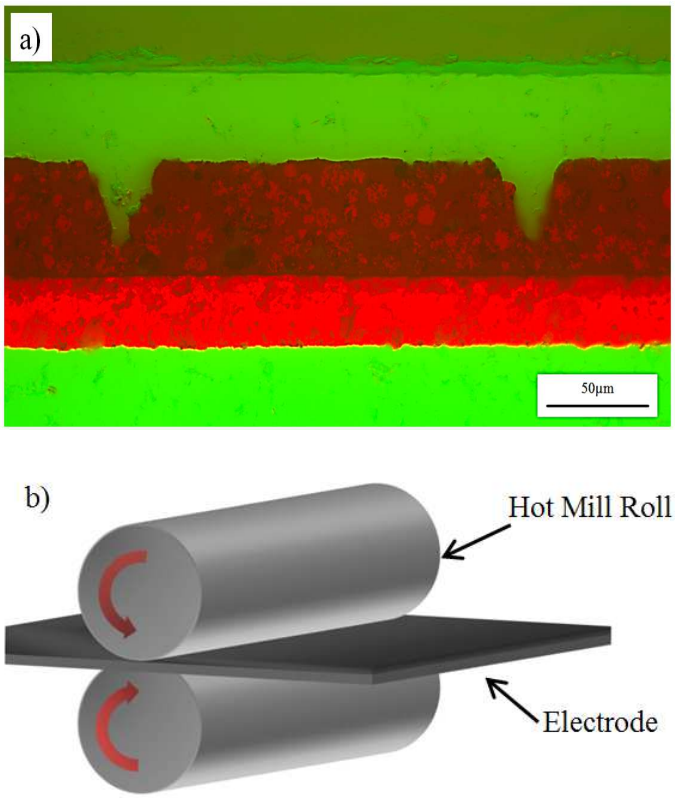

Figure 2: NMC-622 properties and processing: a) cross-section view of a calendered and laser structured thick film NMC-622 cathode and b) schematic view of the calandering process.

B. *Ultrafast laser-assisted structuring of thick film NMC cathodes*

A mass loss of ~8-10% is induced by the ablation process. By applying ultrafast laser ablation a thermal impact into the material can be avoided which is illustrated in Figure 3. There is no damage visible outside or along the laser structured area. Neither material melting nor debris formation could be observed. Both types of material modification would have a

negative impact regarding the electrochemical performance. An uneven electrode surface or material modifications would increase the risk of chemical degradation, lithium plating, and shortcuts during electrochemical cycling.

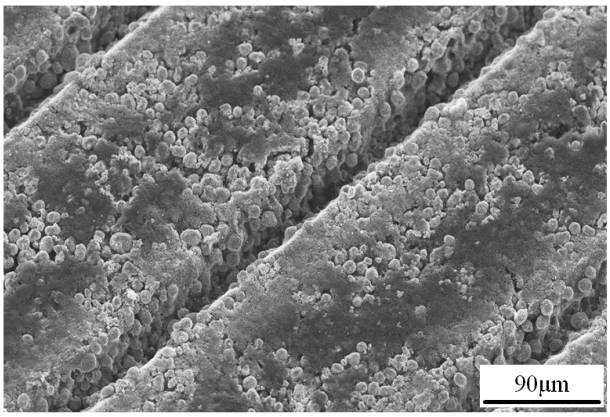

Figure 3: SEM image of a ultrafast laser structured NMC-622 cathode for lithium-ion batteries with a film thickness of 54 µm.

C. Electrochemical characterization of thick film cathodes for lithium-ion batteries

Galvanostatic measurements have been carried out for cells with unstructured and structured NMC-622 thick film electrodes with a film thickness of 54 µm at different charge/discharge rates. A higher initial discharge capacity of 178 mAh/g for cells with laser structured cathodes could be achieved, in comparison to cells with unstructured electrodes, which reached an initial discharge capacity of 171 mAh/g for a C-rate of C/10. The impact of the laser structuring is increasing with increasing C-rates, which could also be shown by Mangang et al. [10] for lithium iron phosphate ($LiFePO_4$) and Pröll et al. [15] for lithium manganese oxide composite cathodes ($LiMn_2O_4$). At a discharge rate of 1C the cell with laser structured electrode shows an discharge capacity which is improved by 6%. At 10C the cell with structured cathode can maintain a discharge capacity of 35% (61 mAh/g) of the initial value, while the capacity of the cell with unstructured electrode drops to 12% (21 mAh/g) of the initial capacity.

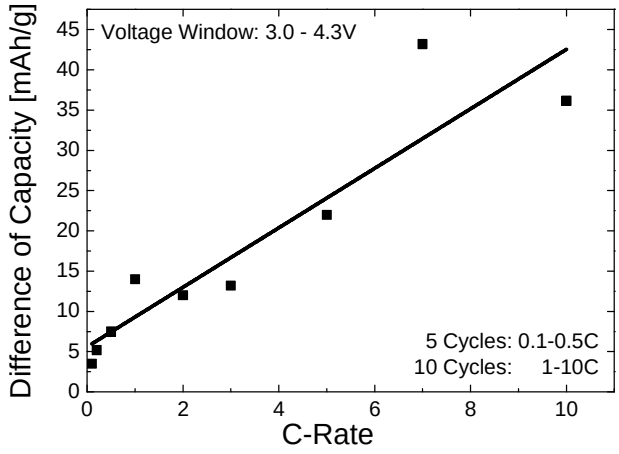

Figure 4: Difference of capacity of cell with laser structured cathode and cell with unstructured cathode (cathode: NMC-622).

III. CONCLUSIONS

Homogeneous electrolyte wetting in thick film electrodes is a main challenge in battery manufacturing which can be significantly improved by introducing capillary structures by using ultrafast laser structuring. Besides an improved wetting, laser structuring can also improve interfacial kinetics due to an increased active surface area, which was shown for cells with structured electrodes revealing an improved discharge capacity of about 23% (10C) in comparison to cells with unstructured cathode material. By this approach, the small material loss due to laser structuring can easily be compensated. High power and high energy properties can be achieved at the same time. The advantages of such an advanced 3D battery concept has to be studied in more detail with focus on a further increased film thicknesses and high energy NMC materials providing a further increased amount of nickel (e.g., NMC-811).

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