3D-cathode design with foam-like aluminum current collector for high energy density lithium-ion batteries

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ABSTRACT

Increasing the area specific capacity and reducing the inactive/active material ratio of cathodes and anodes is considered to be a promising approach to improve the energy density of lithium-ion batteries. In principle, this can be achieved by increasing the thickness and the active material mass loading of the electrodes. However, the fabrication of thick electrodes with good electrochemical performance is challenging regarding the drying process, mechanical stability, electronic conductivity, etc. The application of Al-foams as current collector provides a 3D electronic conductive network, which can host high loadings of active material combined with high mechanical stability. Herein, we demonstrate a slurry infiltration process capable to fabricate cathodes with high active material loading. A variety of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC111) based cathodes with thicknesses up to 260 μm and area specific capacities high as 7 mAh cm^{-2} are investigated comprehensively. The electrodes exhibit good cycle life and rate capability performance due to the unique 3D current collector concept. Even at the 2.0C discharge rate, an area specific capacity of 2.3 mAh cm^{-2} is obtained, which is high in comparison to conventional Al-foil concepts. The design freedom of the presented approach is illustrated by the fabrication of cathodes optimized for high rate capability.

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1. Introduction

Lithium-ion batteries are widely applied in portable electronic devices and their applications expand rapidly, e.g. towards hybrid, all-electric vehicles and stationary energy storage for modern power grids [1]. The rapid increase of these highly functionalized applications strongly demands higher energy and power densities, excellent charge-discharge cycling performance and better safety of the battery device. Typical electrodes for lithium-ion batteries are porous composites consisting of active material particles, binders and conductive additives coated together onto a current collector foil and infiltrated with a liquid electrolyte. The current collectors of the positive and the negative electrodes, typically Al and Cu metal foils, are connected via an outer circuit that can supply an electric consumer. During charging/discharging electrons are transferred between the current collector foil and the individual active material particles within the electrode volume to enable electrochemical oxidation/reduction. To achieve a sufficient electrical contact between the current collector and distant active

material particles, conductive additives, e.g. nano-sized carbon black, are added to the slurry before the preparation of the electrode via a casting process. Both the useable energy density and the rate capability depend heavily on the inner electrical resistance of the electrode, which is mainly influenced by the proportion of conductive additives in the slurry. Increasing amounts of conductive additives increase the rate performance but also decrease the energy density of the overall electrode, since they do not contribute directly to the electrochemical cell reaction. Furthermore, design parameters as electrode thickness, porosity and particle size, lead to complex systems which influence the overall electrochemical properties of the electrode [2,3].

Generally, to increase the energy density of a battery cell, the amount of electrochemically inactive compounds have to be kept to a minimum. This can be achieved by changing the composition of the electrode slurry, e.g. by reducing the absolute amount of binder and conductive additives. Another possibility is to change the electrode design, e.g. reducing the overall porosity (which is filled by electrolyte) or to increase the thickness of the electrode in order to decrease the mass ratio between the inactive current collector and the active material. Especially the increase of the coating thickness has a massive influence on the cell costs. For example, the increase of the film thicknesses of NMC cathodes

from 50 μm to 100 μm results in a cost reduction of 25% as well as in a cell mass and cell volume reduction of 15% [4]. However, these routes of increasing the energy density have substantial drawbacks:

- Reducing the amount of binder degrades the mechanical integrity of the electrode, which limits the process ability (e.g. cutting, winding) and cell cycling stability (risk of electrode delamination).
- Reducing the amount of conductive additives increases the ohmic resistance restricting the rate capability of the electrode (percolation threshold of needed additive).
- Reducing the porosity decreases the effective transport properties (conductivity, diffusivity) of lithium in the liquid electrolyte, which heavily limits the rate capability of the electrode.
- Increasing the electrode thickness elongates the inter-electrode diffusion paths of lithium-ions in the electrolyte and increases the ohmic resistance of the electrode.

Furthermore, the fabrication of thick electrodes with established casting processes (e.g. slot die or tape casting) is challenging in view of achieving defect free electrodes with high material homogeneity, fast drying properties and mechanical stability. NMC111 cathodes based on low amounts of 3 wt.-% PVDF binder and a thickness of 320 μm show poor rate capability with a capacity loss of 37% for C-rates increasing from 0.1C to 0.5C [5]. Furthermore, a significant ohmic loss across the separator, based on 4 times higher current densities at the cathode-separator interface, results in a 18 times higher heat evolution, which may cause safety problems in large format pouch cells. A detailed analysis of the limitations of thick electrodes based on NMC622 cathodes (2.2–6.6 mAh cm^{-2}, up to 154 μm thickness) and synthetic graphite anodes (7.3–23.4 mAh cm^{-2}, up to 182 μm thickness) demonstrates a significant cell degradation due to Li-plating at the anode for current densities larger than 4 mA cm^{-2}. The authors suggest that the maximum attainable capacities for this material combination, even for operation at C/10, are limited to low NMC622 loadings ranging between 2.2 and 3.3 mAh cm^{-2} [6].

A very promising approach toward high energy density electrodes with good rate capability is the application of 3D-designed current collectors, which penetrate the whole electrode volume. Particularly, 3D metal foams can be loaded with a high amount of active material, which allows the reduction of the inactive/active material ratio [7–9]. LiCoO$_2$ infiltrated 3D Al-celmets (highly porous metal foams) demonstrated high active mass loadings of 5–10 mAh cm^{-2} (160–400 μm cathode thickness) and superior discharge capacities in comparison to Al-foil cathodes [10]. Al-foam concepts have the advantage of a much larger surface area, which provides many triple points between active material, metal collector and electrolyte, and consequently reduce the ohmic limitations and the charge transfer resistance [11–15]. In the case of very thick electrode concepts ($\gg$ 200 μm), the metal foam supports the mechanical integrity of the material composite. This leads to a high electrode stability with reduced risk of delamination during cycling. However, kinetic limitations were also reported for ultra-thick metal foam concepts, based on full cell tests with graphite infiltrated Cu-foam (28 mg cm^{-2} graphite loading) and NCM111 filled Al-foam (89 mg cm^{-2} NMC111 loading). With a cathode and anode thickness of 1.2 mm each, after cell formation a reversible storage capacity of 10 mAh cm^{-2} was demonstrated along with a rather poor C-rate capability with a 38% capacity loss from 0.02C to 0.2C [16].

In the present study, we demonstrate a slurry infiltration process capable to fabricate 3D cathodes with high and adjustable active material loading based on thin and highly porous Al-foam sheets of about 300–500 μm thickness. A semiautomatic foam filling and densification method was developed and a variety of LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ (NMC111) based cathodes with thicknesses up to 260 μm and area specific capacities high as 7 mAh cm^{-2} are prepared. The electrochemical performance of the electrodes is investigated in terms of cycle life and rate capability tests showing superior properties compared to conventional foil type electrode concepts. Furthermore, the design freedom of the presented approach is illustrated by the fabrication of cathodes optimized for high rate capability.

2. Materials and methods

2.1. Materials

LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ (NMC111, NM-3100 Toda America, USA) and carbon black (Super P, Imerys, Switzerland) were used as active material and conductive additive, respectively. Polyvinylidene fluoride (PVDF 5130, Solvay, Italy) was used as a binder together with N-Methyl-2-pyrrolidon (NMP 99,5% GPR RECTAPUR®, VWR Chemicals, Germany) as solvent. An Al-foam from Mitsubishi Materials Trading Corp. (MMC Al foam sheets, Japan) with 150 μm average cell size, 0.3 mm and 0.5 mm thickness, with 7.3 mg cm^{-2} and 11.8 mg cm^{-2} respectively, was used as 3D metal collector. Fig. 5 shows the microstructure of the NMC111 granules as well the open pore structure of the Al-foam.

2.2. Electrode preparation

For the preparation of the 3D cathodes, PVDF powder was dissolved under stirring in NMP solvent for 24 h. Subsequently, the slurry was mixed in a dissolver (Dispermat LC, VMA Getzmann, Germany) by adding NMC111 and carbon black powders up to a solid content of 43.8 wt.-%. The ratio of NMC111/carbon black/PVDF was set to 91.8/4.1/4.1 wt.-%. The final slurry showed a viscosity of 0.8 Pas at a shear rate of 20 s^{-1} at 20 °C. The Al-foam sheets were cut into circular samples of 0.5 inch (1.27 cm) size by laser cutting (Fraunhofer IWS, Germany).

The Al-foam samples were infiltrated with the prepared NMC111 slurry by using a custom build semiautomatic dispenser machine from KMS Technology Center GmbH Germany (Fig. 1).

In the process, samples S1 were prepared by placing a 0.5 mm thick Al-foam sample between a sample holder and filter paper (Grade 1, Whatman, USA). With a dispenser unit, 0.2 ml slurry was dosed on top of the sample. Then, the slurry was sucked into the foam volume applying a vacuum of 600 mbar underneath the sample bottom. After one hour resting, the sample was removed, overlapping slurry on top was manually removed and the specimen was dried at 80 °C for 15 h in a laboratory-drying chamber. Finally, the sample was densified in a uniaxial press with 16.9 kN and manually grinded to 260 μm thickness on sandpaper. Alternatively, samples S2 were prepared by dip coating of a 0.3 mm Al-foam sample into the slurry, putting to rest for one hour on a filter paper (Grade 1, Whatman, USA) and finally dried at 80 °C for 15 h in a drying chamber. Comparable samples to S1 and S2 were prepared for microscopy and quality characterization.

As prepared samples were carefully characterized by measurements of weight and size. Based on the mass densities and the composition of the raw materials, the electrode loading, NMC111 active material loading as well as the geometrical porosity of the samples were calculated (Table 1).

2.3. Materials diagnostics

Reference specimen were prepared for SEM and X-ray computed tomography. For SEM characterization, the sample was infiltrated with a polymer resin and cut by a wire saw. Then the