



Intensive powder mixing for dry dispersing of carbon black and its relevance for lithium-ion battery cathodes



Henrike Bockholt*, Wolfgang Haselrieder, Arno Kwade

^a Institute for Particle Technology, Technische Universität Braunschweig, Volkmaroder Str. 5, 38104 Braunschweig, Germany

^b Battery LabFactory Braunschweig, Langer Kamp 19, 38106 Braunschweig, Germany

ARTICLE INFO

Article history:

Received 20 November 2015

Received in revised form 13 March 2016

Accepted 7 April 2016

Available online 13 April 2016

Keywords:

Lithium-ion battery cathodes

Carbon black

Dry mixing

Electrode manufacturing

Electrode structure

Process-property-relation

ABSTRACT

Carbon black is an important component in lithium-ion battery electrodes since it significantly improves the electric conductivity in the coating. Dependent on the carbon black structure and the homogeneity of the carbon black distribution, electrical and electrochemical electrode properties vary. The presented work reveals that the carbon black structure in lithium-ion battery electrodes can precisely be governed by careful parameter variations in an upstream dry mixing process. Significant changes in important electrode properties like mechanical, structural and electrical characteristics are achieved and can be described as functions of the process parameters “mixing time” and “mixing intensity”. The integration of an intensive dry mixing process improves the coating homogeneity and creates short-range electrical contacts on the particle surfaces, leading to enhancements in cycling stability. Long-range electrical contacts can be re-established due to a subsequent calendaring step, compensating rate capability losses, which can be identified for uncalendered electrodes.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Optimized active materials with a high initial capacity and an outstanding performance are the contribution of material researchers to high performance lithium-ion battery cells. Beyond that, it is required that the electrode manufacturing processes and cell assembly steps are able to transfer these initial qualities via various process steps into the product. To minimize production-related losses of the initial material performance a deep understanding of the manufacturing process is essential. However, few is known about the effect of electrode or cell production processes on the resulting physical and electrochemical properties.

One critical process step in electrode production highlighted in this work is the dry mixing of powdery components prior to dispersing them in a solvent. The inclusion of a dry mixing step in the manufacturing chain is not often practiced [1–4] although it can change important electrode properties as we reveal in the present article.

Electrochemically active materials, binders and conductive additives are the important components in both, anodes and cathodes for lithium-ion batteries. Dry mixing of these ingredients can not only be used for a first homogenization but also for fragmentation of the highly branched and agglomerated carbon blacks (denoted as CB in the following). CB (or similar) is commonly used as conductive additive

in battery electrodes [5–7] and is of high importance since it has the possibility to strongly improve electric and even ionic conductivity [8]. An insufficient CB distribution inside the electrode matrix for instance leads to inhomogeneities and thus to unexploited sections, which decreases specific capacity and cycle life [9–11]. The CB desagglomeration behavior is already shown to be strongly dependent on the chosen mixing device [12] since the specific energy input, which is related to mixing intensity and mixing time, varies for different mixers.

It has been reported by Liu et al. [13–15] and others [16,17] that a strong carbon black and binder network and its specific structure inside the electrode is essential for a good electrochemical performance. Cho et al. [3] described that carbon conductives fail to form sufficient electrical pathways without the presence of binder molecules. CB itself is characterized to have a weak ability to form conductive networks around active material particles [10,18], which is disadvantageous for an optimal utilization of active materials' initial capacity. We propose that not only the choice of binder and an optimized CB to binder ratio have to be investigated — the desagglomeration and resulting distribution of the CBs is susceptible to careful variations in processing conditions and, thus, should be taken into account as well.

In the following we reveal the influences of high shear dry powder mixing on structural, electrical, mechanical and electrochemical properties of NMC cathodes. Analyses of all intermediate products, such as powder mixtures, suspensions and electrodes are presented and discussed to make the impact of the dry mixing process as transparent as possible and to allow for a deep understanding of the correlations between process parameters and product properties.

* Corresponding author at: Institute for Particle Technology, Technische Universität Braunschweig, Volkmaroder Str. 5, 38104 Braunschweig, Germany.

E-mail address: h.bockholt@tu-braunschweig.de (H. Bockholt).

2. Experimental

2.1. Materials and recipe

The experiments are designed to reveal correlations between the mode of dry mixing, the different starting electrode materials and the resulting properties of powder mixtures, suspensions and electrodes. Thus, the experiments are carried out restricting the complexity of the material system to a minimum and forgoing diverse possible additives. The composition was limited to three important components: electrochemically active material (AM), conductive additive (CB) and binder (B). The recipe contains 90 wt% of cathode active material $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NMC: NM-3100, Toda Kogyo Group), 6 wt% of Carbon Black (Super P-Li, Timcal Ltd.) and 4 wt% of polyvinylidene fluoride binder (Solef® 1013 PVDF, Solvay Solexis S. p. A.). CB and NMC particles show huge differences in size and morphology: NMC particles are spheres, have a median particle size of $x_{50} = 10 \mu\text{m}$ and show a quite narrow size distribution ($x_{10} = 7.1 \mu\text{m}$, $x_{90} = 14.5$). Its BET surface area is small ($S_{\text{NMC}} = 0.44 \text{ m}^2/\text{g}$) compared to the CB agglomerates ($S_{\text{CB}} = 65 \text{ m}^2/\text{g}$). Carbon black consists of nanoscale primary particles ($x_{50} \approx 40 \text{ nm}$), which form aggregated to 100–300 nm size. Those aggregates are further agglomerated to particle clusters with a few micrometres in size.

For the wet dispersing process *N*-Methyl-2-pyrrolidone (NMP standard grade, BASF SE) was used as solvent. The suspensions are subsequently coated on an aluminium current collector. The active material mass loading for all cathodes is set to $8.1 \text{ mg}/\text{cm}^2 \pm 0.2 \text{ mg}/\text{cm}^2$.

2.2. Electrode manufacturing

2.2.1. Intensive dry powder mixing

All powdery components (AM, CM, B) are dry mixed in this first process step in order to initially form a homogeneous mixture and to additionally pre-desagglomerate the CB. The high intensive shear mixing device (Nobilta™, Hosokawa Alpine AG), is operating with a fixed horizontal mixing chamber (inner diameter: $d_{\text{ch}} = 130 \text{ mm}$), a high speed rotating shaft with attached paddles ($d_{\text{p}} = 124 \text{ mm}$) and a cooling jacket (Fig. 1). In the mixing process the bulk material is centrifuged to the chamber wall due to the fast rotating shaft. Dispersive mixing takes place based on high shear forces, which are introduced to the bulk in the small gap (3 mm) between the paddles and the wall. Only recently this dry mixing device was reported to be used to attach MWCNTs [19] or CB [12,20,21] on NMC surfaces.

The dry mixing using the Nobilta™ was performed as a two-step process. Firstly, the different components (AM + CB + B) are homogenized for $t_{\text{hom}} = 2 \text{ min}$ with a very low circumferential speed of $v_{t,\text{hom}} = 1.75 \text{ m/s}$. This mixture is denoted in the following as “ $t_{\text{mix}} = 0 \text{ min}$ ”. Secondly, the defined fragmentation of the CB agglomerates is realized by distinctly higher speeds $v_{t,\text{mix}}$ for different mixing times t_{mix} . This second step is varied within this study to achieve a deeper understanding of the coherencies between changes in the dry mixing step and the resulting differences in product properties.

The mixing process is carried out with 1000 cm^3 of powder, which is four times the annular gap volume. The weight of the mixer charge is calculated with the bulk density of the mixture $\rho_{b,\text{mix}} \approx 0.75 \text{ g}/\text{cm}^3$ after 2 min of homogenization, measured by volumetric controlled weight analysis.

2.2.2. Dispersing, coating and drying

The dispersing of the powdery mixtures in the solvent was performed in a dissolver (Dispermat CA, VMA Getzmann) with a toothed dissolver disk ($d_{\text{td}} = 50 \text{ mm}$) for $t_{\text{dis}} = 60 \text{ min}$. The tip-speed of the disk was set to $v_{t,\text{dis}} = 9 \text{ m/s}$ and vacuum (10 mbar) was applied for the complete dispersing time after adding the powder, and for another 10 min after dispersing while keeping the suspension in motion, stirring

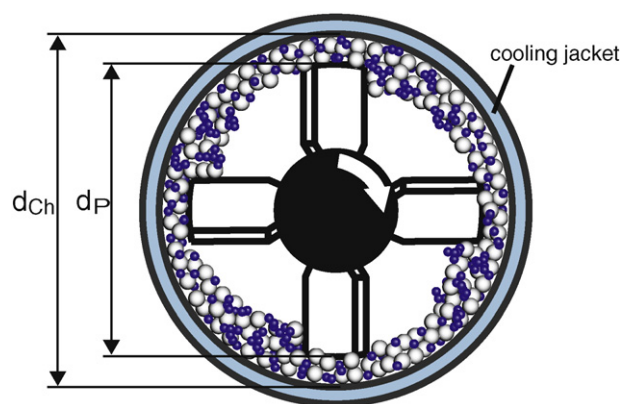


Fig. 1. Schematic drawing of the high intensive shear mixing device Nobilta™.

with $v_{t,\text{dis}} = 1.31 \text{ m/s}$. The solids content for all suspensions was set to $c_m = 0.65$.

For all produced suspensions the parameter set-up for the coating and drying process is kept constant to minimize influences due to the coating and drying process and, thus, to allow for unaffected and comparable analyses of the produced electrodes. The suspensions are coated on an aluminium current collector in a continuous pilot-plant scale coater (LabCo®, Krönert GmbH & Co KG) via a comma bar reverse roll coating system. Using a coating speed of 2 m/min and a three stage convective drying process the temperature profile is implemented as follows: 80 °C, 100 °C and 120 °C for 1 min in each stage.

2.3. Analyses of intermediates and products

The produced powder mixtures are analysed regarding powder conductivity and packing density to identify changes in the mixing result for different processing parameters and to provide information on mixing progress. The measuring of these two characteristic values was set-up in a materials testing machine (Z010, Zwick GmbH & Co. KG) to apply a defined pressure of 1 MPa to the powder in an insulating, cylindrical sample holder. The sample is electrically contacted on both fronts of the powder bulk cylinder. A current of 1 mA is applied and the electrical resistance R_{Ej} in compressed state is calculated from the measured voltage. The packing density ρ_p for the powder bulk pellet is derived knowing the sample weight of 1.5 g as well as the sample holder geometry and the measured powder packing height.

Characterizing the battery suspension concerning its rheological properties enables to draw conclusions about dispersing progress and coating properties. The used rheometer (Bohlin CVO 120, Malvern) is equipped with a cone and plate geometry. The cone is 40 mm in diameter and has a 4° angle. Shear rates are applied stepwise starting at 50 s^{-1} and reaching 500 s^{-1} through in ten linear steps, including a prior temperature equilibration for 150 s and a pre-shearing at 2 s^{-1} for 120 s. The measuring temperature is 20 °C.

It is well known that not only a variation of components but also changes in the manufacturing of electrode suspensions can influence the cohesion of the coating and its adhesion on the current collector [22,23]. Thus, the produced electrodes are characterized regarding coating cohesion strength σ_N with a pull-off test, implemented in a materials testing machine (Z020, Zwick GmbH & Co. KG). Measurement details have already been published elsewhere [24]. Volume resistance measurements are carried out in the same materials testing machine, using circular electrode samples (current collector and coating; $d = 12 \text{ mm}$). Between two conducting stamps the samples are analysed while applying a pressure of 354 kPa and a current of 10 mA. The resistance of the electrode R_{Ej} is measured for 3 s and then averaged.

Electrodes are further characterized by means of mercury intrusion to obtain details on the electrode's structure, particularly on pore diameter distribution and porosity. For this purpose two samples of each

Download English Version:

<https://daneshyari.com/en/article/6676711>

Download Persian Version:

<https://daneshyari.com/article/6676711>

[Daneshyari.com](https://daneshyari.com)