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The interaction of consecutive process steps in the manufacturing of lithium-ion battery electrodes with regard to structural and electrochemical properties



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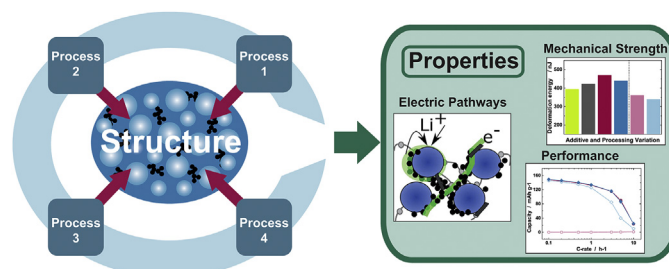
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HIGHLIGHTS

- A concept is presented that explains the complexity of electrode manufacturing.
- The concept derives how processing indirectly affects electrochemical performance.
- Graphite addition enhances performance if long-range electric pathways are missing.
- Calendering can disturb electric pathways, when CB network is mechanically weak.
- Calendering improves performance only if electric pathways are not disturbed.

GRAPHICAL ABSTRACT



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ABSTRACT

The individual steps in the electrode manufacturing process, e.g., conductive additives addition, mixing, and calendering, strongly affect the electrochemical and mechanical properties of the electrodes. LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ (NCM) cathode electrodes with conductive additive variations are fabricated using a reference and an intensive mixing process, and are subsequently calendered to different porosities. It is found that graphite reduces the pore size of NCM electrodes, in contrast to the carbon black that establishes additional nanoscale pores. Electrodes manufactured with reference mixing result in a porous carbon black network with good overall electric pathways, whereas those manufactured with intensive processing result in a dense carbon black network, leading to good short-range contacts, but a lack of long-range contacts. In this case, the addition of graphite as a conductive additive is identified to establish important additional long-range contacts. Due to the structural differences achieved by the compared processing routes, the calendering process can have a positive or negative impact on battery performance.

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1. Introduction

The performance of lithium-ion batteries is known to be strongly dependent on the electrochemical active and inactive materials in the electrode and is also influenced by the fabrication process. Thus, for a long time, researchers focused on the impact of active materials [1–4], recipes [5–20] and choice of conductive additive addition [21–32] on the electrochemical performance of battery electrodes. Furthermore, empirical relationships between variations in electrode manufacturing processes and relevant electrode properties have been published [33–37]. Typically, the physical properties and the electrochemical performance of the composite electrodes are analyzed as a parameter of the mentioned effects. Such direct derivations of relationships are problematic since physical (i.e. structural) changes in the electrode matrix are not taken into account. It is exactly the structure, where the important electrochemical reactions take place, which is mainly responsible for the overall performance of the battery cell [38–42]. The formation of this structure is determined by the choice of the components, the recipe and every single process step in the manufacturing chain. Fig. 1 provides a schematic illustration of the relations between processes, structures and properties in the context of lithium-ion battery electrode manufacturing. Additive addition, slurry manufacturing and calendaring are only three exemplary process steps, which significantly influence the electrode structure. In addition, the coating and drying of the electrodes is as well known to play a significant role concerning component demixing [37]. Knowing how process parameters affect the structure, precise *process-structure functions* f_α , f_β and f_γ (see Fig. 1) can be postulated.

The idea to integrate the physical electrode structure as important information to link process variations and electrode properties is seized in recent investigations [43–47]. This seems to be important since mechanical, electrical and electrochemical properties of battery electrodes are results from the coating structure, as revealed in simulative studies [32,38,48–60]. Such identified relations can be expressed as structure-property functions f_{SP} (see Fig. 1).

In a holistic view, taking the relationships between electrode structure and resulting properties as well as the above described *process-structure functions* f_α , f_β and f_γ into account, comprehensive *process-structure-property relations* Y_{PSP} can be developed. These relations can, for example, describe the electrode structure, which is optimized regarding electrical conductivity, and, in addition, can determine which process parameters in the calendaring process are useful to achieve this electrically optimized structure.

In order to refine this concept, the process steps shall not be considered separately, since a change in one step influences the next. For example, a variation in the additives addition leads to diverging mechanical properties, thus modifying the subsequent calendaring process. In Fig. 1, these impacts are expressed as *process-process interactions* f_a , f_b and f_c , which connect the single process steps. With this information, overarching *extended process-structure-property relations* Y_{PSP}^* (see Fig. 1) can be derived.

The production of battery electrodes is often founded by empirical-based knowledge since relations between process parameter variations and resulting electrode properties are complex. With the help of a systematic development of the above described functions and relations, a targeted production of electrodes with optimized properties seems viable. The results of the presented work are believed to particularly highlight the interactions of consecutive process steps in the manufacturing of lithium-ion battery electrodes.

2. Experimental

2.1. Electrode manufacturing

The composite cathode electrodes were prepared with $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ (NCM; HED™ NCM-111, BASF® SE) as active material (AM), carbon black (CB; C-ENERGY SUPER C65, Timcal Ltd.) and graphite (G; C-ENERGY KS6L, Timcal Ltd.) as conductive additives and polyvinylidene fluoride binder (B; Solef® 5130, Solvay Solexis). *N*-Methyl-2-pyrrolidone (NMP; standard grade, BASF SE) was used as solvent. The recipes providing the information about the components used and their weight ratios are listed in Table 1.

The experiments should give a proper basis to reveal important interactions of consecutive process steps in the manufacturing of lithium-ion battery electrodes with regard to structural and electrochemical properties. Therefore, the NCM cathodes were prepared with variations in added conductive additives (Recipe A, B, C and D; see Table 1 and Fig. 2), using graphite, carbon black or a mixture of these. Recipe A is processed without any conductive additive as a reference. Carbon black and graphite additives show significant difference in size and morphology: Conductive graphite particles exhibit a flake-like structure with a median particle size of $x_{50} = 3.4 \mu\text{m}$. Its BET surface area ($S_{\text{NMC}} = 20 \text{ m}^2/\text{g}$) is smaller than the CB surface area ($S_{\text{CB}} = 65 \text{ m}^2/\text{g}$). Carbon black consists of nanoscale primary particles ($x_{50} \approx 40 \text{ nm}$), which form 100–300 nm sized aggregates. Those aggregates are further agglomerated to particle clusters in a size of a few micrometers.

The suspensions were manufactured under diverging processing conditions. An intensive process, resulting in a strong carbon black desagglomeration and its attachment to the active material surfaces [32,61], is compared to a reference process, in which the different components are only homogeneously distributed. The electrodes were finally compressed to three different porosities (approximately 45%, 35% and 25%) via calendaring at room temperature. Fig. 2 gives an overview on the experiments that were carried out, while details for the single process steps are described hereinafter.

As first step to prepare the suspension, the binder was dissolved in NMP for 30 min and degassed. Depending on the recipe and processing option (compare Fig. 2), different dry mixing techniques were used: “Intensive Dry Mixing” is carried out in a high intensive shear mixing device (Nobilta™, Hosokawa Alpine AG) with a circumferential velocity of the mixing tool ($d = 124 \text{ mm}$) of $v_t = 16.23 \text{ m s}^{-1}$ for 4 min, “Dry Mixing” is processed in a 3D-motion mixer (Turbula®, Willy A. Bachofen AG Maschinenfabrik) rotating with $n = 49 \text{ rpm}$ for 15 min when mixing AM and CB, or 5 min when adding graphite. This mixing step results in a homogenization of the different components, but nearly not in a dispersion of carbon black aggregates.

Subsequently, the powder mixtures were dispersed for 60 min in the NMP-binder mixture using a dissolver (Dispermat CA, VMA Getzmann) with a 50 mm toothed disk. The circumferential velocity of the disk was set to $v_t = 9 \text{ m s}^{-1}$, and vacuum was applied while dispersing. For all suspensions, the solids content was adjusted to $c_m = 0.65$.

The resulting suspensions were coated on 20 μm aluminium foil using a continuous pilot-plant scale coater (Labco, Kroenert GmbH & Co KG) with a comma bar reverse roll application system. The coating and drying speed was set to 2 m min^{-1} , and the temperatures in the convective dryer sections (length: 2 m each) were implemented as follows: 80 °C (section 1), 100 °C (section 2) and 120 °C (section 3). The calendaring process was carried out using the calender device (GKL 400 MS, Saueressig GmbH & Co. KG) at room temperature with a speed of $v_C = 0.5 \text{ m min}^{-1}$.

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