



Influence of dry mixing and distribution of conductive additives in cathodes for lithium ion batteries



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HIGHLIGHTS

- A model is presented that explains the conductivity drop after dry mixing of active material and carbon black.
- It is shown how the conductivity drop can be avoided by an admixture of carbon materials.
- Recommendations are given in order to optimize the carbon distribution.

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ABSTRACT

Conductive additives, like carbon black or graphite, are essential components of lithium ion batteries due to the limited electrical conductivity of most electrode materials. However, there is still a lack of knowledge about the optimized distribution of these materials within the electrode. A dry mixing process is used in order to prepare a conductive coating by depositing carbon black on the surface of $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ (NMC) cathode particles. It is demonstrated that this – from a theoretically point of view – favorable distribution does not allow the preparation of working electrodes without taking into account the role of the binder. After adding an organic binder to the slurry, the polymer deposits on top of the carbon shell during drying and inhibits the conductive contact between the particles. This can be avoided by a fraction of distributed carbon particles which are associated with the binder phase providing conductive paths through the isolating organic material. It is shown that carbon black and graphite are principally fulfilling this task, but both materials are leading to varying processing behavior and electrode properties.

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1. Introduction

Electrodes of lithium ion batteries (LIB) primarily consist of a particulate electrochemical active material (AM) that is mixed with electro-conductive additives and a polymer binder. The polymeric component is added to bind the particles together and to fix these on a metallic current collector foil. The conductive additives are necessary in order to compensate the limited conductivity of most electrode materials. Especially the poor electrical conductivity of common cathode materials (ranging for commercial materials from 10^{-9} S/cm for LiFePO_4 to 10^{-3} S/cm for LiCoO_2 [1]) hampers the

electronic transport through the composite which is essential to provide the overall charge neutrality during the charge transfer.

Carbon black (CB) or graphite powders are usually chosen as conductive additives at the cathode side [2]. Although other types of conductive fillers with a higher aspect ratio, like carbon fibers or carbon nano tubes, have a lower percolation threshold and are more effective to form conductive pathways between multiple particles [3,4], carbon black is still preferred due to its slurry stabilizing capability [5], high chemical inertness and low costs [6]. The role of graphite is slightly different as the conductivity enhancing potential is less marked due to the larger particle size and the plate-like morphology. However, graphite is also an efficient compaction aid that allows improving the direct particle contacts throughout the electrode, providing also a lower electrical resistance and a higher energy density [6–8].

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Carbon black is delivered as a powder with low bulk density. It consists of colloidal particles with a primary particle size below 100 nm, which are chemically bound to form aggregates with a more or less complex structure [9]. The aggregates themselves form agglomerates which are held together by weak physical forces, e.g. van-der-Waals forces, forming branched clusters with a size up to the micron range. Within the electrode, the carbon black must be distributed in order to produce continuous conduction pathways from the current collector to each particle of the active component with a minimum of added amount. As the particle size of many active materials is in the range of 10 μm , it is also beneficial to provide supplementary contact points and cover the particle surface with additional conduction paths. It is a common agreement in literature and in practice that the carbon black clusters must therefore be broken into much smaller fragments which have to be homogeneously distributed within the electrode. But, although theoretical and experimental studies already have been carried out to investigate the influence of the spatial distribution of the conductive aids [1,10–24], there is still a lack of knowledge about the optimized distribution and the therefore required processing routes of the carbon black which also takes into account the other components within the electrode.

From a theoretical point it should be beneficial to deposit the carbon black particles as a thin coating on the surface of the active material [25]. In this configuration only a small amount of conductive additive is required to provide an electrical connection between all particles. Dominko, Drogenik and coworkers e.g. propose a homogenous coating of the carbon black particles by fixing them on the surface of the active material with the help of gelatin [26,27]. With such uniformly distributed carbon black it was demonstrated for LiCoO_2 cathodes to yield better performance for merely 2 wt.% of carbon black as with 10 wt.% of non-uniformly distributed conductive aids [28]. However, in their investigations the electrodes were only pressed and did not contain an additional binder phase. The binder is necessary to provide good mechanical strength and sufficient adherence to the current collector in order to prevent disintegration of the particles during cycling [29].

An alternative to produce a carbon coating on the active material can be realized by high-shear dry mixing. In this process a blend of active material and carbon black is agitated by peripheral paddles with high speeds whereby the blend is centrifuged to the outer shell, getting stressed in a small gap between the shell and the paddles [30,31]. Compared to a commonly used planetary mixer, a dry mixer reveals a number of process-related differences. Mainly, two effects influence carbon black crushing and distribution during the process. First is the excessive specific energy input of the dry mixer and the resulting high mechanical stresses in the mode of compaction, shear, and impact. Such conditions induce tens of thousands of collisions per second for a particle with comparable impact strength in both the normal and tangential direction [32]. Second is a crushing effect of the carbon black caused by the active material (analogous to ball mills). Due to this, comprehensive deagglomeration of the carbon black and the achievement of a homogeneous mixing state is possible. With increasing load and stress duration, more and more fragments are adhering to the surface of the active material, forming a layer around the particles. After appropriate energy input even mechanofusion occurs, i.e. penetration of the fines into the open pores of the larger particles and thermo-mechanical induced fusion of particles, forming a dense shell of carbon around the active material [33]. In this paper the consequences of this process for the manufacturing of LIB electrodes are investigated, i.e. properties and processing of the slurries and the electrical and electrochemical behavior of the electrodes are presented.

2. Experimental

2.1. Electrode and cell preparation

$\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ (NM-3100, Toda America, USA) with a mean particle size of 8.9 μm , measured by electroacoustic spectrometry (DT1200, Dispersion Technology, USA), and a BET surface of 0.4 m^2/g , (measured by Flowsorb II 2300, Micromeritics, USA), was used as the active cathode material (AM). Carbon black (Super C65) with a BET surface of 62 m^2/g and a mean TEM primary particle size of 35 nm [17] was acquired from Imerys Graphite & Carbon, Switzerland.

Dry mixing of the active material and the carbon black was performed in a Nobilta NOB-130 (Hosokawa Micron Corporation, Japan). Maximum loading with this machine is 250 g of powder. In the current investigation fixed rotation speeds at 3600 min^{-1} or 4000 min^{-1} and mixing intervals up to 70 min were chosen.

Slurries, electrodes and cells were prepared in order to investigate the influence of the dry mixed powders on the electrode manufacturing process and on the properties of the final product. First of all, a polyvinylidene difluoride (PVDF) binder (Solef 5130, Solvay Solexis S.p.A., Italy) was dissolved in N-methyl-2-pyrrolidone (Sigma Aldrich, Germany) at ambient temperature. The dry mixed particle blend was dispersed in the PVDF solution in a vacuum equipped dissolver (VMA Getzmann, Germany) for 30 min at a maximum speed of 2000 min^{-1} . The resulting base slurry contains around 92 wt.% of $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ (NMC), 4 wt.% of carbon black and 4 wt.% of PVDF binder with a solid content (NMC + CB) of 22.5 vol.%.

Furthermore the influence and necessity of additional conductive material was investigated. Therefore, an extra of up to 5 wt.% untreated carbon black or up to 10 wt.% of graphite powder (Timrex KS6L, Imerys Graphite & Carbon, Switzerland, mean particle size of 3.4 μm and BET surface of 21 m^2/g), was added to the base slurry in the dissolver mixer.

Reference slurries were prepared by mixing untreated AM and CB powders directly in the dissolver mixer. Without a preceding dry mixing, the slurries were found to yield a much higher viscosity. Hence, the solid content had to be reduced by additional solvent down to 18 vol.% in order to get a slurry that can be operated for electrode preparation.

Electrodes were cast on a 20 μm thick aluminum foil using a continuous coater (KTF-S, Mathis AG, Switzerland) with knife coating device at a gap of 200 μm and a speed of 0.2 m/min. The electrodes were dried in a first stage at 80 $^\circ\text{C}$ air temperature, followed by a second stage at 120 $^\circ\text{C}$, in each case for 5 min. Compaction of the electrodes was done in a heated calendar at 60 $^\circ\text{C}$ with adjusted clamping force so that an electrode porosity around 30 vol.% was achieved.

Pouch cells with ceramic coated separator foil (Separion[®], Evonik, Germany) and graphite anode were prepared for electrochemical tests. Electrode size was 50 \times 50 mm^2 for the cathode and 54 \times 54 mm^2 for the anode. Before assembling all electrodes and separators were dried overnight in a vacuum furnace at 130 $^\circ\text{C}$. All pouch cells were assembled in a dry room at a dew point of -50 $^\circ\text{C}$ to -60 $^\circ\text{C}$. The electrolyte was 1 M LiPF_6 /ethylene carbonate (EC) + diethyl carbonate (DEC) (1:1 by weight ratio) obtained from BASF, Germany. After assembling, all cells were stored around 20 h at 40 $^\circ\text{C}$ to facilitate a homogeneous distribution of the electrolyte within the electrodes.

2.2. Characterization

Electrical resistivity of the AM/CB blends was measured in a compaction tool with metallic punches and an isolating die. By

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