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Influence of formulation method and related processes on structural, electrical and electrochemical properties of LMS/NCA-blend electrodes

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ABSTRACT

The impact of different formulation methods, involving related process technologies, as well as the influence of dispersing intensity on the structural and electrical coating layer properties of $LiMn_2O_4$/$LiNi_{0,80}Co_{0,15}Al_{0,05}O_2$ (LMS/NCA) blends are studied. Findings are finally correlated with the electrochemical rate-capability in order to derive process-structure–property functions to facilitate systematical electrode development. LMS was found to be sensitive according mechanical stress but by processing LMS/NCA blend electrodes this problem can be avoided. In general carbon black (CB) agglomerate size and its distribution in the binder network were identified to be significant factors influencing rate-capability. Both were found to influence pore structure by utilizing representative low and high energy methods for the formulation of the suspensions. The specific pore volume in the pore size region of 10 μm $\geq d_p \geq$ 0.5 μm was discovered to strongly influence rate-capability. These highways for lithium-ion transport allow for higher mass of lithium-ions per unit time penetrating into the inner surface of the coating layer. Specific volume and thus rate-performance can either be increased by a binder solution based formulation method or by decreasing the specific energy input during dispersing process. Hence no superior formulation method exists. The adjustment of mixing intensity and therewith the achieved CB agglomerate size, referring to the formulation method used, is essential. Thus comparable electrochemical rate performance was found for the same specific volume of approximately 0.25 cc g^{-1} but for different dispersing intensities. Further, the pore size region of 1.5 μm $> d_p >$ 0.03 μm was identified to be characteristic for the CB agglomerate size and the corresponding CB treatment method used. Peakedness of the pore size distribution was found to follow electrode conductivity which was the largest for a distributive dry mixing method. For electrodes showing a good CB agglomerate distribution in the binder network rate-capability was found to be limited by the pore structure of the coating layer and, thus, preliminarily by the corresponding ion transport kinetic. Based on the findings a model concept on processes occurring during dispersing was proposed and discussed to describe viscosity evolution over dispersing time.

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Nomenclature

AM	active material
BS	binder solution
CB	carbon black
DbDM	distributive dry mixing
HEV/PHEV	hybrid electrical vehicle/plug-in hybrid electrical vehicle
HiDM	high intensive dry mixing
LMS	$Li(Li-Mn-Al)_2O_4$
NCA	$LiNi_{0,80}Co_{0,15}Al_{0,05}O_2$
NCM	$LiNi_{0,33}Co_{0,33}Mn_{0,33}O_2$
PVdF	polyvinyliden fluoride
$x_{10,3}/x_{50,3}/x_{90,3}$	characteristic parameters of particle size mass distribution

1. Introduction

Active material blend electrodes, containing a high power performance capable lithium manganese spinel (LMS) [1,2] and a layered oxide material (NCA) [3–6] are subject of recent investigations. Blending active materials (AMs) opens up for material- and electrode manufacturing as well as battery system optimization. Regarding the battery system optimization for a specific battery application the combination of these both materials is of high interest for the design of HEV and PHEV batteries since power and energy capability of the electrodes can be adjusted by varying the amounts of active materials fulfilling the specific application needs. Due to kinetic limitations regarding electrical and ionic transport, power and energy density performance of an electrode, containing a single active material, is always a trade of coating layer thickness, respectively electrode's mass loading. From a material point of view it could already be shown that for specific blend ratios of LMS and NCA the manganese dissolution from the spinel [7,8] as well as the exothermic reaction behavior of NCA in a thermal runaway reaction [3,9] can be suppressed nearly entirely [10]. Both properties are extremely important according battery cell aging behavior and material intrinsic safety of the cell. Especially the negative safety properties of NCA [9,11] led to a low acceptance of this AM in the automotive industry.

This paper addresses the influence of process technologies and formulation strategies on the mechanical, structural, electrical and finally electrochemical properties of LMS/NCA blend coating layer properties. Overall scope of this research study is to contribute to the development of process–structure property functions. This correlation of primarily structural and electrical coating layer properties with electrochemical rate-performance opens up for systematic optimization. Object of optimization is the hierarchical solid state structure of the CB/PvDF-binder network in which the AMs are embedded. Therefore, representative low and high energy processes were chosen to address different types of CB treatments and, thus, different CB agglomerate sizes achievable. Introductorily Section 3.1 gives an overview on basic electrode properties. In Section 3.2 the influence of the mechanical stress on the LMS and NCA will be discussed comparatively to blended electrodes. This is done based on experiments using a high intensive dry-mixing method. Based on this a comparative analysis on selected formulation methods for LMS/NCA blend electrodes, involving different process devices, is conducted in Section 3.3. The selected

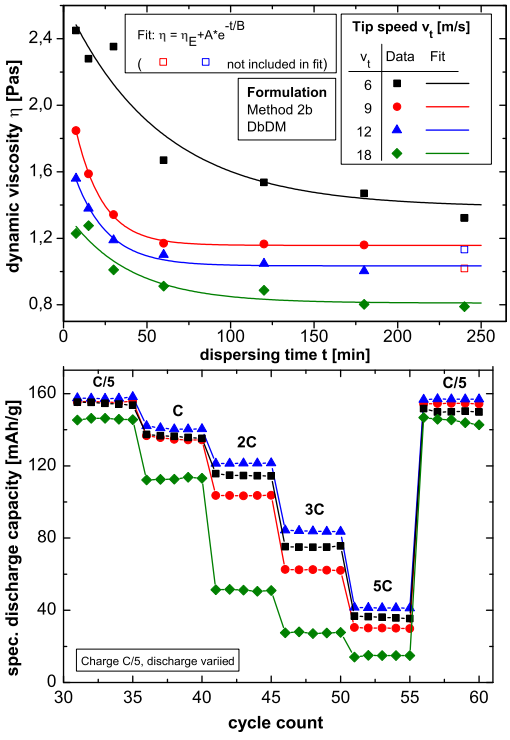

Fig. 1. Progress in viscosity over time and achievable final viscosity for NCA suspensions shown with their corresponding rate-capabilities.

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