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A novel slurry concept for the fabrication of lithium-ion battery electrodes with beneficial properties

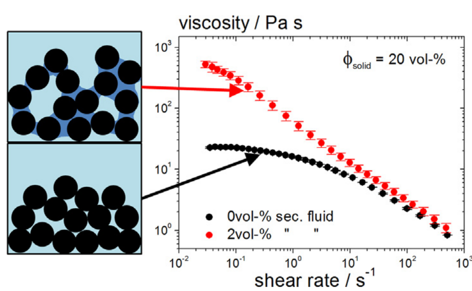
Boris Bitsch [a,*], Jens Dittmann [a], Marcel Schmitt [b], Philip Scharfer [b], Wilhelm Schabel [b], Norbert Willenbacher [a]

[a] Karlsruhe Institute of Technology, Institute for Mechanical Process Engineering and Mechanics, Gotthard-Franz-Str. 3, 76131 Karlsruhe, Germany
[b] Karlsruhe Institute of Technology, Institute of Thermal Process Engineering, Thin Film Technology, Kaiserstr. 12, 76131 Karlsruhe, Germany

HIGHLIGHTS

- We present a new slurry concept based on capillary suspensions for Li-ion electrodes.
- The slurry viscosity in the low shear region is tunable in a wide range without further additives.
- The slurry viscosity in the high shear region remains unchanged which is desirable during coating.
- Storage stability and shape accuracy during coating are improved significantly.
- Good mechanical and electrochemical properties of the novel electrodes are shown.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel slurry concept for the fabrication of Li-ion battery electrodes focusing on water based formulations is presented. Taking advantage of capillary forces inferred by adding a small fraction of a second fluid immiscible with the bulk continuous phase the low shear viscosity can be varied in a wide range without conventional polymeric rheology control agents disturbing the electric properties of the dry electrode. The new slurries provide superior storage stability and excellent shape accuracy of the final dry film. This reduces waste cut-off at the edges and increases the density of active ingredients, thus improving cost-efficiency. The viscosity at high shear rates remains unaffected, thus the slurries can be processed and coated using established equipment and process parameters. Adhesion to the conductor foil and electrochemical properties of the electrode layers and corresponding cells are similar to those made from conventional slurries.

1. Introduction

The performance of lithium-ion batteries is strongly dependent on the electrochemical characteristics and the fraction of active material in the electrodes. However, the fabrication process also plays an important role since it determines the distribution of active material and the structure of the electrode layers.

* Corresponding author. Tel.: +49 721 60848824; fax: +49 721 60843758.
E-mail address: boris.bitsch@kit.edu (B. Bitsch).

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Optimization of the fabrication process leads to the cheaper production of electrodes with improved properties like capacity, cycleability, safety, toxicity and cost [1].

Typically, slurries for lithium-ion electrodes consist of a solvent, the anode or cathode active material, carbon black to ensure the electrical conductivity and a binder for the cohesion between the particles and the adhesion of the electrode layer to the current collector respectively. Furthermore, water based slurries generally contain rheology control agents to adjust the flow properties according to the demands of the respective coating operations.

In general, the process chain for electrode manufacturing is distinguished by its complexity and the large number of influencing factors: the first step is the dispersion of the solids in the solvent to receive a processible and homogenous slurry. This slurry is coated in the subsequent step on the current collector followed by the drying and calendering of the electrode layer. The chosen technology and parameters for mixing and coating as well as the drying and calendering [2] conditions determine the slurry homogeneity, the electrode thickness, the mechanical stability or the porosity of the electrode layer. Therefore, the electrode processing has direct influence on the electrode performance. Beyond that, the characteristics of the chosen active material and additives, the mixing sequences, ingredient ratios and potential additional pretreatment steps of the solids (e.g. dry mixing) have also a strong effect on the electrode performance [1].

The electrode slurry plays a central role in the fabrication process: the flow behavior of the slurry is determined by the ratio of raw materials, the mixing procedure and the mixing sequence. Furthermore, the viscosity function and the sedimentation stability of electrode slurries are factors with superior relevance to the subsequent coating process [3].

Although there are several publications related to the processing of lithium-ion electrodes, the literature focusing on rheological properties of electrode slurries and its optimization is scarce. Kim et al. [4] and Lee et al. [5] discussed the effects of different mixing sequences on the rheological properties of NMP-based cathode slurries and its consequences on the dried electrode. In aqueous anode slurries, Lee et al. investigated the influence of sodium carboxymethylcellulose (CMC) focusing on concentration and degree of substitution [6]; further Lee et al. examined the slurry viscosity depending on the fractions of styrene butadiene rubber (SBR) and CMC [7]. With rising CMC concentration the slurry viscosity increases drastically whereas the addition of SBR does not have a significant effect on the flow properties of the slurry. Beside its major effect on the slurry rheology, CMC also contributes to the mechanical stability of dry electrodes [8].

In the present work, we introduce an innovative slurry concept for the fabrication of lithium-ion electrodes based on capillary suspensions. By adding a small amount ($\sim$1 vol%) of a secondary fluid, that is immiscible with the primary fluid, the flow properties of the suspension can be changed drastically [9]. This general physical phenomenon is found in various kinds of material systems [10]. By adding a secondary fluid to a suspension, an existing sample-spanning network (e.g. van-der-Waals) may be reinforced or such a network is created due to capillary forces introduced by the secondary fluid [11,12]. The corresponding change in flow properties can be utilized to match the specific needs of a certain downstream process unit, in our case the coating of the electrode slurry on the metallic current collector foil.

The coating of homogenous films with constant layer thickness is a key challenge for industrial electrode fabrication. But not only a constant thickness at the center of the electrode layer needs to be achieved, also the shape of the sidewise edges plays an important role. Blurred edges have to be cut-off in order to guarantee for a constant amount of active material per unit area. However, at the position of the take-off lug the edge cannot be cut-off and may lead to a local excess voltage due to the reduced amount of active material at this point. Moreover, depending on slurry rheology and coating conditions local superelevations at the layer curb, so-called “heavy edges”, may occur with major disadvantages for the subsequent fabrication steps.

Superelevations lead to inhomogeneous pressure distributions during calendering resulting in a non-uniform porosity and area capacity of the electrode. Furthermore, regarding production on industrial scale, up-winding of hundreds of electrode layers superelevations add up to several millimeters and provoke undesirable folds in the electrode foil [13]. For these reasons, a good accuracy of the edge shape is of superior importance for industrial electrode processing.

Here, we want to evaluate the novel slurry concept based on capillary suspensions as a cost saving fabrication method for industrial electrode production. We target on an increase of the slurry viscosity at low shear rates in order to fabricate layers with superior coating properties, i.e. sharper edge contours; finally aiming at a reduction of cut-off waste and therefore lower production costs. Furthermore, the concept shall be used to improve sedimentation stability of the slurry. The utilized secondary fluid evaporates during coating and does not remain in the dry electrode layer. The capillary suspension concept is intended to enable a reduction of organic additives like rheological additives and binders, thus allowing higher active material density and better electric conductivity of the electrode layer. Due to similar viscosity data of capillary suspensions at high shear rates in comparison to conventional slurries the application of established coating equipment is possible.

Capillary forces control the formation and strength of the network based on secondary fluid bridges between the particles. The three-phase contact angle $\theta_{S,B}$ is defined as the angle of the secondary phase (S) against the solid surface while surrounded by the bulk fluid (B). Depending on $\theta_{S,B}$, two general states can be distinguished: if $\theta_{S,B} > 90^\circ$ the secondary phase does not preferentially wet the particles and therefore forms droplets surrounded

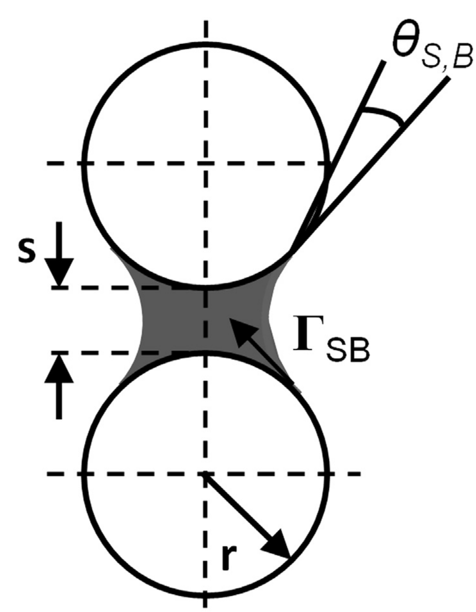

Fig. 1. Schematic drawing of two spherical solid particles connected by a liquid drop in the pendular state giving the essential parameters. The contact angle $\theta_{S,B}$ determines if the admixture is in the pendular state ($\theta_{S,B} < 90^\circ$) or capillary state ($\theta_{S,B} > 90^\circ$).