



Investigation of film solidification and binder migration during drying of Li-Ion battery anodes



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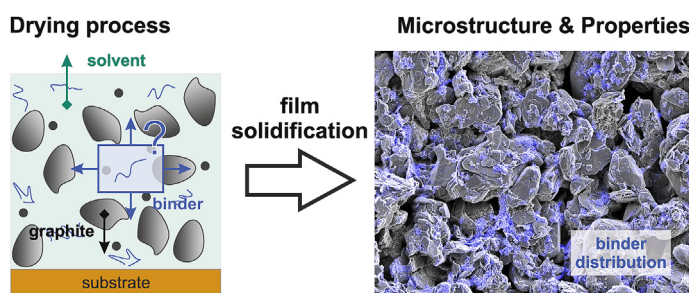
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HIGHLIGHTS

- Insight into the property-determining drying and solidification of electrode films.
- Characteristic drying stages are revealed by a new experimental approach.
- High drying rates trigger binder gradients throughout electrode films.
- A top-down consolidation mechanism based on capillarity and diffusion is proposed.
- The impact of drying rate on electrochemical properties is revealed.

GRAPHICAL ABSTRACT



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ABSTRACT

The property determining micro-structure of battery electrodes essentially evolves during drying, appointing it a paramount, yet insufficiently understood processing step in cell manufacturing. The distribution of functional additives such as binder or carbon black throughout the film strongly depends on the drying process. A representative state-of-the-art model system comprising graphite, polymeric binder, carbon black and solvent is investigated to gain an insight into the underlying processes. A new experimental approach is introduced that allows for revelation of the evolution of binder concentration gradients throughout the film during drying. Binder is detected by means of energy-dispersive x-ray spectroscopy (EDS) at the top and bottom surface. Drying kinetics is investigated and the impact of the drying process on electrochemical performance is disclosed. The enrichment of binder at the surface, which is observed while applying high drying rates, is shown to depend on two fundamental processes, namely capillary action and diffusion. The findings reveal characteristic drying stages that provide fundamental insights into film solidification. Based on that, a top-down consolidation mechanism capable of explaining the experimental findings is disclosed. Adhesion of the active layer to the substrate is shown to strongly depend on the local binder concentration in the vicinity of the substrate.

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1. Introduction

Thin, functional films produced through coating and drying of particulate dispersions are widely spread in a plurality of

applications such as paper coatings [1–3], latex films [4–6] or lithium-ion battery electrodes [7,8]. The latter has been intensely discussed in recent years in particular and many improvements have been achieved, for instance by the introduction of new active materials or binder systems [9,10]. It is widely accepted in all of these applications that the process steps required for film production in general and the drying in particular are of paramount importance for film properties, which are governed by the film's internal structure or morphology [1,11–14].

Against this background it is quite remarkable, that only few publications in the field of battery coatings are addressing the complex interrelations of processing and film properties. While the effect of mixing [15–19] and the mixing tool [15,20] are at least somewhat reviewed, the coating [21,22] and drying [7,8,11,12,23] steps are hardly discussed. Likewise, the calendaring is only focused on in few publications [24,25]. One reason may be the extent of process control along the whole process chain from mixing to calendaring, which is an essential requirement for granting reproducible investigations into a single process step [26]. As a matter of course, this is also true for the evaluation and introduction of new battery materials.

Two driving forces prevail in research on lithium-ion battery electrodes: Cost reduction and improvements in energy density. The latter objective is mainly addressed in research on new materials. But especially the manufacturing has great potential to contribute to the aspired progress. The electrode film comprises active material particles and additives like disperse or soluble binder and conductivity-enhancing nanoparticles such as carbon black. An optimized electrode microstructure features a maximized active material content and a functional distribution of additives. A fundamental understanding of the governing processes occurring during electrode manufacturing and their impact on component distribution can therefore contribute to the establishment of improved mixing, coating, drying or calendaring processes.

Regarding the manufacturing costs, an increase in throughput would be desirable. At present, the drying process constitutes the major bottleneck in production speed. An increase in production speed is inevitably linked to an amplification of dryer capacity and therefore investment costs. The promotion of a better understanding of the governing processes occurring through the various stages during drying is obligatory to increase the potential of state-of-the-art dryers by engineering customized drying profiles.

The evolution of the electrode's micro-structure occurs exceedingly during drying [6–8,23]. As mentioned above, publications on the drying step are scarce with respect to lithium-ion battery material systems. Consequently, film solidification and mechanisms that influence film structure are hardly discussed. On the contrary, paper and latex coatings have been subjected to intensive research in the past decades, which has resulted in a fairly sound understanding of film solidification and the mechanisms affecting film properties [6,27–33]. Although some major differences become obvious when comparing both applications, the findings might nevertheless be adopted and could possibly form the basis for models that describe film solidification in battery electrode films and drying dispersions in general. This hypothesis is supported by analogies found regarding the binder migration, which was observed previously in publications on coated paper [2,29], latex [6,33] as well as in battery electrode drying [7,8,23].

This work illuminates the underlying processes occurring during solvent removal that significantly govern the final film properties. A new experimental approach is developed for this purpose. The basic concept comprises the consecutive adjustment of a high (HDR) and a low drying rate (LDR) in a single isothermal drying step and the assessment and comparison of

anode films produced under variation of the transition between the two drying rates that therefore exhibit different drying histories. The approach exploits the stronger extent to which binder migration occurs under harsh drying conditions [8] and, thus, allows for identification of the evolution of binder concentration gradients throughout the film. The experiments are conducted under well-defined boundary conditions that allow for interpretation of the drying kinetics. The evolution of binder gradients is evaluated on the basis of the binder concentration at the free surface and the interface between the active layer and the substrate after delamination by means of energy-dispersive x-ray spectroscopy (EDS). In addition, adhesive force to the substrate is introduced as indirect measure for the local binder concentration in the vicinity of the substrate. The findings provide an insight into the fundamental solidification mechanism of anode films. As a result, a model based on capillarity and diffusion is presented that describes film formation and component distribution depending on the drying boundary conditions. Electrochemical tests of selected anode films are presented, which underline the important role of the drying process in terms of electrode quality.

2. Experimental

2.1. Mixing

After dry pre-blending of commercial graphite (SMG-A, Hitachi Chemicals, Japan, $d_{50} = 20.4 \mu\text{m}$) and carbon black (C-ENERGY C65, $d_{50} = 65 \text{ nm}$, Imerys Graphite & Carbon, Bodio, Switzerland), the binder solution comprising Polyvinylidene fluoride (PVDF; Solvay Solef 5130, Brussels, Belgium) and *N*-Methyl-2-pyrrolidone (NMP; Carl Roth) was added stepwise at a polymer mass fraction of 5.55% to reduce carbon black agglomeration, thereby following the recommendations given by Terashita and Miyanami [34] and Lee et al. [16]. At the final solid content the slurry was homogenized and degassed under vacuum. The mixing process was conducted in a laboratory dissolver equipped with a custom-built mixing tool enhancing vertical transport. A more detailed description of the mixing procedure is provided in the [supporting information](#). The composition of the final dispersion and the dry films are listed in [Table 1](#).

2.2. Coating

Both coating and drying were conducted in a custom-built setup comprising an impingement dryer and a temperature-controlled aluminum plate ([Fig. 1](#)).

Films 60 mm wide and 80 cm long were applied on 10 μm copper foil (Nippon Foil Mfg. Co. Ltd., Tokyo, Japan) by knife coating at a speed of 10 cm s^{-1} . Both dryer and aluminum plate were operated at a constant temperature of 76.5 °C. The doctor blade as well as anode slurry were pre-heated to the same temperature prior to film application. The mean area loading of the dry films and the average dry film thickness were $70.5 \pm 1.7 \text{ g m}^{-2}$ and about 78 μm , respectively.

Table 1
Composition of dispersion and dry film in mass fractions.

	Dispersion $x/[-]$	Dry film $x/[-]$
Graphite (Hitachi)	43.5	91.7
Carbon black (C65)	1.4	2.8
Binder (PVDF)	2.6	5.5
Solvent (NMP)	52.5	–

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