Critical electrode properties and drying conditions causing component segregation in graphitic anodes for lithium-ion batteries

Bastian G. Westphal[a,b,c], Arno Kwade[a,b,c,*]

[a] Institute for Particle Technology, Technische Universität Braunschweig, Volkmaroder Straße 5, 38104, Braunschweig, Germany
[b] Battery LabFactory Braunschweig (BLB), Technische Universität Braunschweig, Langer Kamp 19, Braunschweig, Germany
[c] Lion Engineering GmbH, Rebenring 33, 38106, Braunschweig, Germany

ABSTRACT

Among others, the performance of lithium-ion batteries is determined by the structure and material distribution of the electrodes. These electrodes are known to develop an inhomogeneous inactive material distribution during drying of the wet-coated film. The segregation of the conductive additive and the binder was found for the graphite anodes studied in this work and was proven by indirect and direct analyses. Segregation reduces the adhesion strength between coating and substrate and increases the electrical resistance as well as the elasticity of the anode. It was found by spectroscopic analysis that binder concentration and by association carbon black concentration increase from bottom to top of the coating. This Segregation increases with drying temperature and the amount of solvent that needs to evaporate. An auxiliary parameter is introduced to determine a combined, critical value for the driving force of the solvent evaporation (drying temperature) and the anodes' mass loading. Finally, the mass loading and/or the drying temperature to avoid segregation can be estimated with regard to the final product and the existing drying equipment.

1. Introduction

The use of lithium-ion batteries started in the consumer electronics section where cameras and mobile phones have been equipped with lithium-ion batteries since the early nineties followed by their use in all kinds of power-tools and finally in electric vehicles. The properties of the battery cells and its components (casing, positive (cathodes) and negative electrode (anode), separator, electrolyte) steadily improve with the growing performance requirements [1]. Very decisive for the performance of the final battery cell is the structure of the both electrodes. The production of lithium-ion battery cells is a long and complex process chain with numerous operating and disturbance [1]. The presented research studies the drying process of the electrode production as a critical process step for achieving high performance of lithium-ion batteries.

The aforementioned positive and negative electrode in lithium-ion batteries consist of a thin porous coating (30–150 μm) on a thin metal substrate (8–20 μm). Such coatings are usually composed of an active material (AM) and at least two inactive materials (IM), a polymeric binder (B) and a conductive additive (CB) in varying ratios [2,3]. The actual lithium-ion intercalation takes place at the surface of the active material [4], whereas the binder and the conductive additive provide

mechanical strength and electrical contact [5–9]. The electrode's production process exerts a major impact on its microstructure, as production is responsible for the degree of dispersion [10–15], interaction between the different species [16–18], material distribution along the cross-section [19–26] and porosity of the coating [27–31]. This work studies the drying process of lithium-ion battery anodes as it plays a key role regarding the distribution of inactive materials along the anodes' cross-section [20–26,32]. Furthermore, it is a cost driver concerning investment and energy costs [33], as typical industrial dryers need to be likely 100 m long to provide sufficient drying time (1–2 min [1,34,35]) as coating speed exceeds 50 m/min.

Drying is mandatory to evaporate the solvent and create an adhering, dry coating on the substrate. Fig. 1 visualizes the process of drying, which is generally divided in at least two stages (first and second drying stage). Solvent evaporation leads to a loss in volume accompanied by film shrinkage and thus approaching of particles (cf. Fig. 1, A), which are drawn together by capillary forces. A relative movement between the active material and the inactive material as well as a solvent flow towards the surface of the coating change the distribution of the inactive material. Further solvent evaporation drives the active materials to form a porous particle network with a fully filled pore network (cf. Fig. 1, B). This stage is followed by a retreat of the
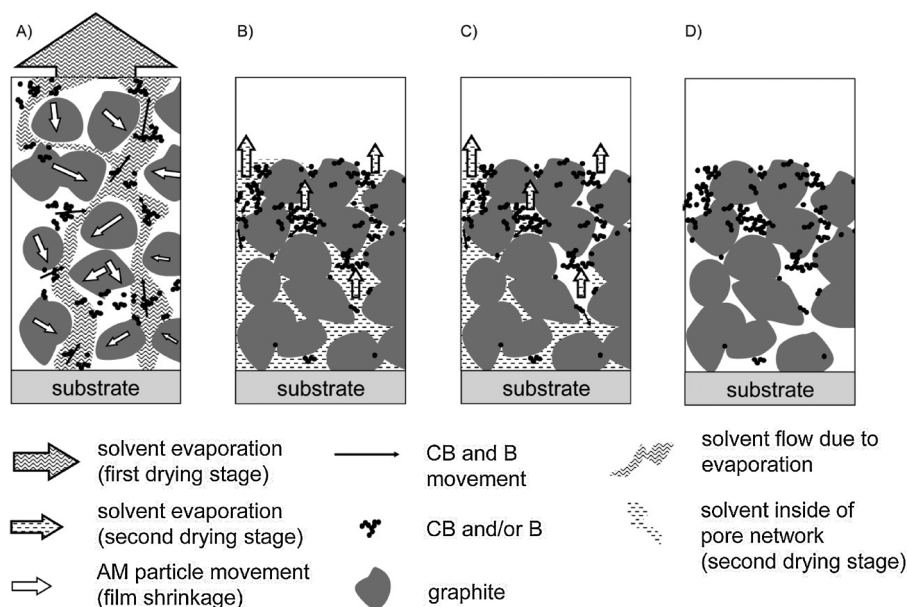
Fig. 1. Simplified representation of the drying process. Particle and solvent movement during first and second drying stage, caused by solvent evaporation and film shrinkage.

liquid-gas interface inside the particle network (cf. Fig. 1, C). The narrow pores of the active material backbone and the retreating liquid-gas interface impede the segregation of inactive materials during this stage. Jaiser et al. show that the retreat of the solvent does not follow a horizontal drying front, thus, surficial pores still exist beyond the point of fully saturated pores, leading to a constant rate period that obliterates the difference between first and second drying stage, which are classically determined by constant and falling drying rate, respectively [31]. Fig. 1, D shows the final electrode when segregations of the inactive materials occurs during drying. The binder and the carbon black accumulate at the electrodes surface leading to a depletion at the interface of coating to substrate.

The segregation has been reported for paper [36] and pharmaceutics [37] and has been proven for lithium-ion battery electrodes as well [21–26]. The migration is an unwanted process as electrical and mechanical properties of the electrode deteriorate. A binder gradient with an increasing binder concentration from substrate to surface was found for CMC and PVDF binder and different active materials [19,22–26]. All authors agree that higher driving forces for solvent evaporation (more intense drying) enhances segregation, whereas moderate drying conditions help to avoid segregation. Jaiser et al. suggest a drying profile with intensive drying conditions in the initial and the final stage separated by a low intensive drying regime to achieve a homogenous material distribution [32]. They determine a characteristic intermediate drying stage, which is sensitive for binder migration. However, there is no focus on the avoidance of segregation considering electrode properties and drying conditions simultaneously. This is of interest because commonly the mass loading m_A is used to adapt the electrode's properties to the purpose of the cell. For example, thinner (lower mass loading) electrodes are much more suitable for high power applications as they provide shorter transport distances for the charged species [38–41]. Obviously, the final mass loading of a dried electrode depends on the wet mass loading and the solids content of the suspension, which together determine the total solvent content that needs to be evaporated during drying. As the total solvent content and drying conditions both influence drying time, it is necessary to research its influence simultaneously with changing drying parameters. The modification of the solids content is unwanted in most industrial applications as it is a change in the product rather than in the process. Furthermore, the dispersing device requires a specific solids content to provide sufficient

shear forces in order to achieve an efficient dispersing process. Additionally, the coating device limits the viscosity of the suspension, as pumping and distribution in the slot die need to be homogeneously. The scope of this work is to find drying temperatures T_D that avoid a segregation at a desired final electrode mass loading, or the other way around to design a dryer that is sufficient to produce the desired electrodes without segregation of inactive material.

A change in active to inactive material ratio serves to study the suitability of the analysis to determine changes in inactive material concentration caused by segregation. Segregation is studied in dependence on drying temperature and mass loading of the electrode, via several indirect mechanical and electrical methods. The results are confirmed by direct laser-induced breakdown spectroscopy (LIBS) and energy dispersive x-ray spectroscopy (EDX), which is used to quantify the degree of segregation. Finally, a critical combination of solvent content and temperature is derived, which leads to segregation and, thus, deteriorating electrode properties. Although drying time is obviously affected by drying temperature and mass loading, it is inadequate to describe the effect on segregation, since drying temperature and mass loading have a contrary impact on drying time. An enhanced temperature leads to faster solvent evaporation and, thus, faster fixation of the electrode's structure thereby shortening the time for any segregation gradient to establish. Therefore, an auxiliary parameter is introduced to describe the enhancing effect of drying temperature and mass loading (absolute amount of solvent, AAS) on the degree of segregation.

2. Experimental

2.1. Materials and electrode composition

CMS G10 mesophase graphite serves as active material (AM) and was obtained from Shanshan. Solef 6020 polyvinylidene fluoride (PVDF) serves as binder (B) and was obtained from Solvay Specialty Polymers. Super P carbon black (CB) serves as conductive additive and was obtained from Timcal. N-methyl-2-pyrrolidone (NMP) from BASF serves as solvent. The ratio of AM/CB/B in the dry powder mixture is 91/3/6 wt.%. The solids content in the suspension is 58 wt.% during dispersing.