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Regular Article

Experimental investigation into battery electrode surfaces: The distribution of liquid at the surface and the emptying of pores during drying

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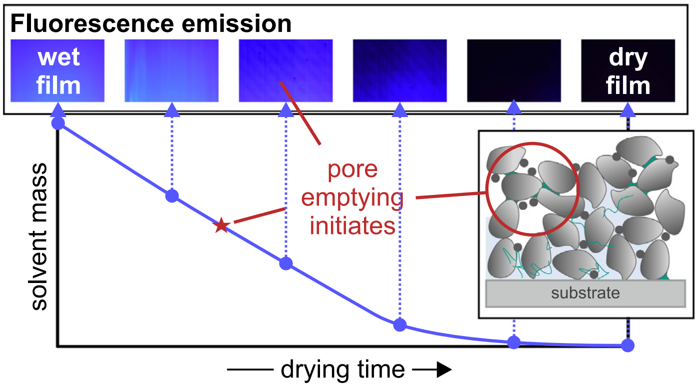
GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: Drying constitutes a key step in the production of thin, particulate films as the complex microstructure develops and functional additives redistribute throughout the film, thus shaping the film properties. The onset of pore emptying constitutes a paramount marker in the film formation process as capillary liquid transport emerges.

Experiments: Film shrinkage, development of surface liquid content and liquid depletion in surface pores of thin films are studied by means of a novel experimental approach, using the example of lithium-ion battery anodes. An optical brightener is incorporated into the films, which are produced in a convective slot-nozzle dryer. After various drying times, images of the film, which emit light fluorescently during exposure to UV-A radiation, are captured and analyzed by image processing. Film shrinkage is observed by means of a laser displacement sensor.

Findings: As soon as the first pores empty, pore fluid is transported convectively. By exerting an external force, i.e. a pressure surge, on the film, the transition from a fully saturated to a partially emptied film is revealed. The significance of drying rate and particle shape are studied. We show that liquid depletion in surface pores can occur both prior and concurrent with the end of film shrinkage.

1. Introduction

Particulate coatings take a key role in a plurality of applications including paper coatings [1–3], latex films [4–11], lithium-ion battery electrodes [12–19], ceramic green tapes [20] or membranes

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Abbreviations: PVDF, polyvinylidene fluoride; NMP, N-Methyl-2-pyrrolidone; DSBB, Disodium 4,4′-Bis(2-sulfonatostyryl)biphenyl; SLR, single lens reflex.

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for desalination by means of capacitive deionization (CDI) [21]. These types of layers are often applied in the wet state as homogeneous, thin films on various substrates. The solvent is removed in a subsequent (convective) drying step [22].

The properties of such layers are determined by their complex microstructure. In the case of lithium-ion battery electrodes, functional additives are incorporated into the film to improve the mechanical integrity or conductivity. The former is provided by the addition of a soluble polymeric binder [16–18] or a polymeric latex dispersion [12–14], while the latter is provided by carbon black, a nanoscale agent providing additional conductive paths for electron transport [23–25]. Although the initial solid volume fraction in the wet film typically adds up to about 30%, the film still experiences a more or less pronounced shrinkage as solvent evaporates. During the film shrinkage regime, the solid constituents in the wet film approach each other and finally form the solid, porous structure that will form the backbone of the dry film. Capillary forces work at the three-phase boundary where liquid menisci are pinned and significantly exert influence on the evolution of the microstructure. As film shrinkage is completed, the pores deplete and the gas-liquid interface recedes into the porous structure with further solvent evaporation until the film is dry. The functional additives possess a high mobility and redistribute throughout the film during film shrinkage and during solvent evaporation from the pore structure. A phenomenon well known is binder migration. For high drying rates both soluble [17] and disperse binder [12–14] tend to be present in concentrations above the average in the vicinity of the film surface, where evaporation is taking place. On the contrary, low drying rates result in balanced binder distributions. Binder migration represents an undesired phenomenon in battery electrode manufacturing, as a local accumulation of functional additives results in decreased concentrations somewhere else in the film, for instance at the interface between the active material layer and the substrate. An outcome of this is a decreased adhesion between active layer and substrate for films dried at high drying rates [15–17]. More severely, inhomogeneous binder distributions also impact on the electrochemical performance of cells that comprise electrodes due to an increase in internal resistance and the associated deteriorated rate capability [17]. Due to the strong dependency of electrode properties on the drying conditions, solvent evaporation represents a crucial step in electrode manufacturing.

Another issue spotlights the drying process to an even stronger extent. Solvent evaporation is intrinsically tied to huge energy expenditure, as it is conducted in extensive roll-to-roll dryers. This makes the drying step of battery electrodes a decisive cost factor [26,27]. In recent years, industrial coating speeds typically ranged between 25 and 50 m min^{-1} but have increased further. For typical drying times of one to two minutes, vast dryers are required, as both the coating and the drying step are conducted in series in a single plant. The capital investment could therefore be significantly reduced if the drying process could be sped up.

Unfortunately, an ordinary increase in drying rate due to an increase in drying temperature or the gas-side mass transfer is not feasible, due to the aforementioned decline in electrode properties. The good news is that drying is not a linear process but rather a sequence of drying stages that exhibit individual dependencies on the conditions. In a previous publication we reported on the existence of an intermediate drying stage, which is characterized by a strong sensitivity to high drying rates [17]. This stage is confined by two stages that allow for adjustment of high drying rates. A multi-zone drying profile, developed based on these findings allowed for a significant reduction of the required drying time, while crucial electrode properties could be maintained to a level comparable with films that were dried at significantly lower drying conditions [28]. This example is evidence that a sound scientific understanding of the fundamental processes that occur during drying helps to immediately helps to overcome current limitations. These processes for instance include film shrinkage, pore emptying and binder migration.

This work introduces an experimental approach that allows measurement of the film shrinkage, the surface liquid content and the depletion of surface pores of electrode layers during convective solvent removal under drying conditions that include drying rates in the range typically covered by industrial processes. An optical brightener is added to state-of-the-art anode slurries in small amounts, thereby allowing for observation of the liquid phase of the film by means of a camera, as the liquid phase fluorescently emits blue light when being exposed to UV-A radiation whereas the dried parts show no fluorescence. Image processing provides a measure for evaluation of the surface liquid content and therefore for tracing of liquid depletion in surface pores. In parallel, the wet film thickness is tracked by a two-dimensional laser displacement sensor. The findings are deployed to reveal a characteristic event, namely the onset of depletion of liquid in surface pores.

2. Materials and methods

2.1. Mixing

5.55. parts polyvinylidene fluoride (PVDF; Solef 5130, *Solvay*, Belgium) were dissolved in 94.45 parts N-Methyl-2-pyrrolidone (NMP; Carl Roth) by a magnetic stirrer over-night at room temperature. Electrodes with two commercially available graphite active materials (Graphite 1: SMGP-A, *China Steel Chemical Corporation*, Taiwan, $d_{50} = 8.9\ \mu m$, spherical shape; Graphite 2: SMG-A, Hitachi Chemical, Japan, $d_{50} = 20.4\ \mu m$, polyhedral shape) were investigated in this study. Depending on the experimental variation parameters, one of the two graphite powders was dry-blended with carbon black (C-NERGY C65, $d_{50} = 65$ nm, *Imerys Graphite & Carbon*, Switzerland) in a laboratory dissolver (DISPERMAT CN10, *VMA Getzmann,* Germany) at 200 rpm for two minutes. A multi-step dilution process was applied to adjust a good dispersion of the solid constituents [29,30]. In a first dilution step a solid content of 57% was adjusted by addition of PVDF solution. The metal cup containing the slurry components was placed in a double-walled container fed with cooling water to prevent the slurry from excessive heating. The components were mixed at 500 rpm for 10 min. In a second dilution step, the final solid content of 47.5% was adjusted by further addition of polymer solution and pure NMP. The slurry was homogenized for 30 min at 1500 rpm. Vacuum was applied in order to degas the slurry and to improve the coating quality by preventing coating defects that could result from air bubbles in the slurry. The composition of the dry film was 91.7% graphite, 2.8% carbon black and 5.5% PVDF. The slurry was stored over night to allow for constant rheological properties of the slurry to develop [22]. Prior to the coating, an optical brightener (Disodium 4,4′-Bis(2-sulfonatostyryl)biphenyl; DSBB) was added to the slurry at a concentration of 0.1 wt.%. DSBB re-emits blue light after absorbing ultraviolet light.

2.2. Experimental setup – coating and drying

A custom-built batch-coating and drying setup was deployed to produce thin, porous graphite layers. As the applied setup was introduced comprehensively in a previous publication [17], the interested reader is encouraged to consult the detailed description for further information. At this point, merely a short summary is given. The additional installations that were used in the present work are described in full detail.