Binder migration during drying of lithium-ion battery electrodes: Modelling and comparison to experiment

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HIGHLIGHTS

- A model for the evolution of binder concentration within a drying electrode.
- Model predicts undesirable accumulation of the binder for high drying rates.
- Strong agreement between model and experimental results is demonstrated.
- Drying rates small enough to maintain homogenous binder distributions are identified.
- Protocols to minimize drying times and concentration gradients are discussed.

ARTICLE INFO

ABSTRACT

The drying process is a crucial step in electrode manufacture that may lead to spatial inhomogeneities in the distribution of the electrode components resulting in impaired cell performance. Binder migration during the drying process, and the ensuing poor binder coverage in certain regions of the electrode, can lead to capacity fade and mechanical failure (*e.g.* electrode delamination from the current collector). A mathematical model of electrode drying is presented which tracks the evolution of the binder distribution, and is applicable in the relatively high drying rates encountered in industrial electrode manufacture. The model predicts that constant low drying rates lead to a favourable homogeneous binder profiles, whereas constant high drying rates are unfavourable and result in accumulation of binder near the evaporation surface and depletion near the current collector. These results show strong qualitative agreement with experimental observations and provide a cogent explanation for why fast drying conditions result in poorly performing electrodes. Finally, a scheme is detailed for optimisation of a time-varying drying procedure that allows for short drying times whilst simultaneously ensuring a close to homogeneous binder distribution throughout the electrode.

1. Introduction

Lithium-ion batteries are currently used to power the vast majority of portable electronic devices, such as cell-phones, laptops, and tablets, and are growing in popularity for use in hybrid and electric vehicles [1]. While one of the biggest challenges in lithium-ion battery research is to increase the energy density of batteries, another equally important challenge is to optimize the manufacturing process to improve long-term cycling performance and capacity lifetime while keeping control of the manufacturing costs [2–4]. One particularly sensitive step in cell production, which determines the final quality of the battery pack, is the manufacturing process for the electrodes [5,6].

Typically, electrodes are manufactured by coating a current collector with a slurry mixture comprised of active material (AM) particles, conductive carbon nanoparticles, polymer binder (commonly polyvinylidene fluoride (PVDF)) and solvent (commonly N-Methyl-2-pyrrolidone (NMP)) [5–8]. This mixture is then dried (i.e. the solvent evaporated) by exposure to one or more of the following: air flow, heat, a reduction in ambient pressure or radiation [5,6,9–11]. State-of-the-art industrial processes typically rely on convective impingement driers which dry films in only a few minutes [12]. The mixture preparation and coating steps prior to drying have to be carefully executed in order to ensure good electrode performance. For instance, it has been shown that slurry mixtures prepared by a multi-step process lead to a more

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uniform distribution of AM and carbon particles, resulting in less electrode polarization and better cycling capability [7,8]. In addition, since the slurry is often stored for considerable periods of time before drying, it must be stable to sedimentation, particularly of the relatively large electrode particles. Such stabilisation may arise from various causes including repulsive electrostatic interactions or the formation of a polymer gel state [13]. For an extensive review on mixture preparation the reader is referred to [14].

The most frequently used coating method in industry is slot-die coating, in which a liquid is poured into a die that deposits the coating liquid onto a rolling substrate belt. Coating defects such as film instability and edge effects can occur and need to be controlled which can, *e.g.*, be achieved by varying the coating speed and the gap ratio [15,16]. In contrast, many research-grade electrodes are manufactured by manually spreading the slurry on the substrate using a doctor blade. The use of NMP as a solvent is also highly costly and replacing it with aqueous solutions would both reduce the cost of electrode production and be more environmental friendly [17].

Drying begins once the current collector has been coated with the wet particulate electrode mixture. The AM particles are in suspension in the mixture whilst the binder is dissolved in the solvent. In the first stage of the drying process (*film shrinkage*) solvent evaporates from the top surface of the film causing it to shrink, until the rigid AM particles make contact with each other stopping any further decrease in film thickness. This initiates the second stage of drying (*pore emptying*) in which the solvent in the pores between the AM particles evaporates. Transport of binder in the film shrinkage stage is believed to be more significant than in the pore emptying stage [6,12] because, during pore emptying, capillary effects lead to a disconnection of the pore network (large pores empty before smaller ones) and consequently to the development of isolated regions of solvent.

Electrode drying has been the subject of intense experimental research in recent years [5,6,9,12,18–22] and a consensus has developed that changes to the drying process parameters (temperature, air-flow, pressure and radiation intensity) significantly affect the final electrode microstructure and hence the electrochemical and mechanical properties of the electrode. High temperatures and drying rates have been observed to lead to accumulation of binder at the evaporation surface and corresponding depletion close to the current collector [5,9,19,20]. The consequences of a non-uniform binder distribution include lower adhesion of the electrode to the current collector [5,6,9,20], increased electrical resistivity [5,22] and decreased cell capacity [6]. Chou et al. [23] conclude that even though binder makes up only a small fraction of the electrode composition, it plays a very important role in the cycling stability and rate capability of the electrode. In a recent experimental investigation of the effects of drying on binder distribution by
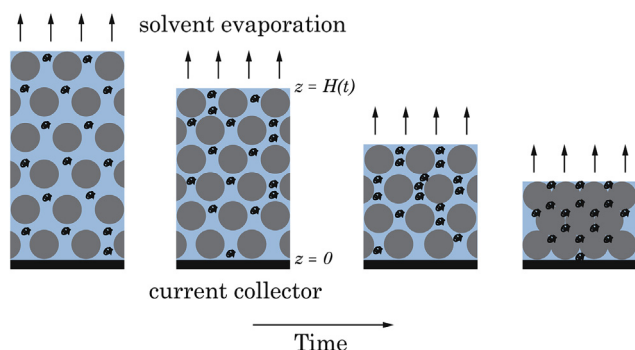
Fig. 1. Illustration of the drying process of an electrode film sitting on top of a current collector. The blue background represents the solvent (which evaporates from the top surface of the film), and the black and grey particles represent the polymer binder and AM particles respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Jaiser et al. [6] it was suggested that the electrode film consolidates by the formation of a dense layer of electrode particles, or 'crust', on the drying surface which then grows down until it reaches the current collector. This hypothesis has since been contradicted by the results of Forouzan et al. [21] and by a follow-up study by Jaiser et al. [12] which both indicate that, as film shrinkage occurs, the electrode particles remain homogeneously distributed.

In both [6] and [12] it was found that rapid removal of the solvent causes an enrichment of binder in the upper regions that cannot be compensated by diffusion at high drying rates. We note also the work of Stein et al. [22], on very slow drying of cathode films, which shows drying rate dependence of the binder distribution.

Theoretical models detailing the physical mechanisms governing the drying of single-component and two-component colloidal suspensions are studied in Refs. [24,25] and [26,27], respectively, while drying of polymer solutions is investigated in Refs. [28,29]. However, to the best of our knowledge, the process of (industrially relevant) fast drying suspensions composed of electrode particles in a binder solution has not been properly tackled before.[1] The aims of this work are to: (i) model this process, (ii) to compare the model predictions to experimental results, and (iii) to use the model to predict optimal drying strategies. In the next section we formulate and solve a simple model for the mass transport of solvent and binder during the film shrinkage stage of electrode drying. In agreement with the results in Ref. [12] we take the electrode slurry to be stable to sedimentation of the electrode particles. In §3, we present solutions to the model, in realistic parameter regimes and for different drying rates and protocols, before discussing techniques for optimising the drying process. Finally, in §4 we draw our conclusions.

2. Problem formulation

We formulate a one-dimensional model in which mass transfer occurs only in the z-direction (perpendicular to the substrate). All model equations are defined for $z \in [0, H(t)]$, where $H(t)$ is the position of the top of the electrode film, see Fig. 1. We track two material phases: a liquid phase (both solvent and dissolved binder), with volume fraction ϕ_l, and a solid phase (AM particles), with volume fraction ϕ_s. The highly electronically conductive carbon black additive (which makes up only a very small fraction of the electrode volume at around 1%) is not treated as a separate phase. Instead, its presence is accounted for by incorporating its volume into that of the binder.

We assume no spatial gradients in temperature throughout the film, justifying this assumption by noting that the least (thermally) conductive constituent of the film, the NMP solvent, has a thermal diffusivity of around m² s⁻¹ (where λ, c_p and ρ, represent the thermal conductivity, heat capacity and density of NMP respectively [30–32]). This leads to an estimate of the time required to reach thermal equilibrium of around 0.1 s which is very much shorter than the (~1 min) drying timescale (the addition of the more conductive materials only serves to further justify this assumption).

As discussed in Ref. [13], electrode slurries are generally stabilised so as to stop the sedimentation and aggregation of AM particles. This leads us to expect the AM particles to be uniformly distributed throughout the electrode film during the drying process, an assumption that is borne out by the images of particle distributions at different stages of drying presented in Ref. [12]. We do not specify the exact physical mechanism responsible for stabilisation, noting that it could be electrostatic repulsion or as a result of a polymer gel state.

It remains to specify a model for the transport of the PVDF binder particles. These particles are typically very small and therefore are

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[1] Stein et al. [22] present some modelling results but their relevance to electrode slurries is not entirely clear because volume fractions of the different phases are not specified properly.