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Micro-structure evolution and control of lithium-ion battery electrode laminate

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ABSTRACT

The electrochemical performance of lithium ion battery (LIB) is strongly affected by the micro-structure of its electrode laminate. A comprehensive understanding of the micro-structure evolution in LIB electrode laminate fabrication process can help to further improve its property. Here, recent progress involving slurry making, coating and drying process in electrode fabrication process is reviewed. The interaction mechanism among particles of active material and conducting additive and polymer molecular in different solvent environment is discussed in detail. And ways to control and improve the electrode micro-structure are proposed. Not only LIB, this review will also provide hints and instructions to other kinds of electrochemical energy storage devices such as supercapacitor, Li-S and Li-air battery.

Contents

1. Introduction

Electrode laminate fabrication process is one of the most important steps in lithium ion battery (LIB) industry. Typically, the electrode laminate of LIB can be seen as a kind of polymer-based composite material, in which active materials and conductive additive particles function as the fillers. During the fabrication process, both active materials and conductive additives are transformed from discrete solid particles into a continuous porous electrode laminate through slurry making, coating and drying process sequentially. The polymer binder is used to provide adhesive force between the electrode laminate and the current collector, as well as bridging all particles together. From the porous electrode theory, the micro-structure of the electrode, such as the thickness (mostly less than 300 μm) [1–3], the local porosity (about 0.3–0.4)[4,5] and the tortuosity of the pore structure[6–9],

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can directly affect the electrochemical performance of LIB[10–20]. At the same time, homogeneous micro-structure must be also controlled in the electrode fabrication process, because of the fact that the variations of those parameters in the whole electrode range [18,21–24] will cause the LIB property decay and failure [25]. Therefore, the micro-structure is usually optimized according to the final application requirements of the LIB, especially for the ones used in electric vehicles [1,26–28]. Unlike the active material synthesis process, the electrode fabrication process is a physical process without any chemical reaction. However, many of the scientific problems hiding behind this process are still not fully investigated. Therefore, tracking the evolution of the micro-structure during the electrode laminate fabrication process and controlling it to optimize the porous electrochemical process is a very important work.

In this article, recent advances in the LIB electrode fabrication process are reviewed and the detailed particle/polymer interacting mechanism hiding behind this process is especially discussed. Furthermore, methods to control and improve the electrode micro-structure are also summarized and compared. It will help to provide new ideas for further development of the industrial LIB fabrication process. And considering the similarity of electrochemical energy storage devices, it can also offer hints for fabricating other devices such as, supercapacitor, Li-S and Li-air battery.

2. Slurry making: from solid particle to fluid suspension

Slurry making is the first step to make the electrode laminate, through which solid particles of active material and conductive additive, polymer dispersant and binder are dispersed in solvent to form a kind of suspension. The state of the slurry hence greatly affects the micro-structure of the final electrode. As for an ideal slurry, active material and conductive additive particles should be dispersed homogeneously in solvent, without coagulation or sedimentation. So, homogeneous dispersion is very important in slurry making process. Fig. 1 shows the particle-polymer interaction in aqueous slurry [29]. According to the DLVO theory, which is usually used to describe the particle interaction in aqueous suspension, the van der Waals attractive forces among the solid particles will bring agglomeration and sedimentation. And hence dispersant polymers are normally required to provide electrostatic repulsive or steric force to de-agglomeration the particles. Fig. 1a shows those forces motioned above.

Besides the dispersion, the rheological behavior of the slurry should also be optimized to meet the requirements of the following coating process. That is, the slurry should maintain stable state without sedimentation [30,31], and at the same time, the viscosity optimization of the slurry is also required for the coating process. Fig. 1b and 1c describe the particle/polymer interaction forces which can keep the well-dispersed slurry stable and modify its rheological behavior through weak gel structure, respectively. Through increasing the viscosity of the slurry, the particles mobility in the dispersion can be reduced effectively and hence the slurry stability improves [13]. However, the high viscosity should be limited at low shear rate case only, or it will bring defects in coating process. Some kinds of weakly coagulated state, which can be easily broken under high shear stress during the coating process, is required.

Therefore, choosing appropriate dispersant polymer is the principle work in the slurry making process. And hence, the particle-dispersant polymer interaction and the stability mechanism in the slurry is investigated widely.

2.1. Characterization methods

When investigating the dispersion state and the resulting micro-structure of the slurry, the most common used characterization methods involve rheological characterization, zeta potential, Cryo-SEM, sedimentation and dispersant adsorption experiments, which can be found in Fig. 2.

2.1.1. Rheological behavior

Rheological property is widely used to investigate the internal structure and dispersion state of particle-polymer system [32–35]. In the rheological field, shear stress at different shear rate is recorded and the viscosity can be calculated by the Eqs. (1) and (2). If the particles are not well dispersed with each other, solid or gel-like behavior will be found by the rheological characterization due to the presence of strong bonding among particles. Instead, when the slurry is dispersed well, a fluid-like behavior will appear and the viscosity will become much lower.

$$\tau = \eta \cdot \dot{\gamma} \tag{1}$$

$$\dot{\gamma} = \frac{dv}{dy} \tag{2}$$

τ: shear stress, η: viscosity, $\dot{\gamma}$: shear rate, v: flow rate, y: distance.

The viscosity of the slurry usually changes with the shear rate, and this phenomenon can give much more detailed description of the particle-polymer interaction in the slurry. When a shear-thinning behavior is present, soft agglomerates which are easily broken by the shear stress are expected to be present. Oppositely, a shear-thickening phenomenon usually indicates that the strong agglomerated particles. When a frequency sweep is applied, the dynamic viscoelastic properties of the slurry system can give the information whether the slurry is fluid or solid-like state, based on the relative value of storage modulus and loss modulus [29].

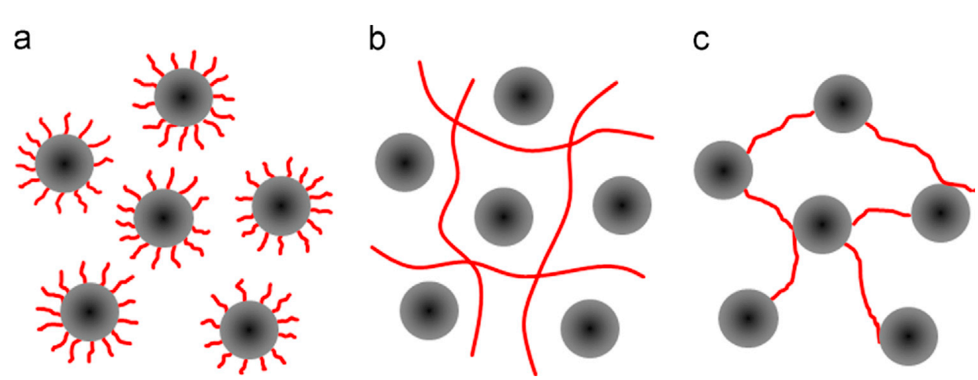

Fig. 1. Different kinds of particle-polymer dispersant interaction mechanism in slurry [29]. (a) electrostatic repulsive and/or steric force for de-agglomeration, (b) viscosity enhancement to overcome settling and (c) gel structure.