

Stability of cathode slurry for lithium-ion battery



Introduction

Lithium ion batteries have applications in laptops, mobile phones, cars and even airplanes as they offer a high energy density and low self-discharge. However, aqueous cathode slurries are subject to strong particles agglomeration leading to an alteration of the mechanical properties of the electrode and a shorter shelf life. Polymers such as Poly(acrylic acid) (PAA) are classically used to improve the particles stability by adsorption. In this application note, stability of cathode slurry was investigated for dispersions of LiFePO_4 (LFP) and Carbon Black (CB) particles supplemented with PAA in function of the pH to understand polymer adsorption effect on stability

KEY BENEFITS

FAST
OBJECTIVE
SENSITIVE

Reference

Effect of pH on the dispersion stability of water based cathode slurry with poly(acrylic acid) as a binder, Kim Do Hoon, Master report from Seoul National university, South Korea.

Battery electrode slurry stability challenges

Electrode coating slurries are complex systems, which contain a large percent of solid particles of different chemicals, sizes and shapes, dispersed in a highly viscous media. Cathode slurry contains active material, conductive agent, binder and solvent. However these components can present various challenges:

- Preparation of the electrodes for the rechargeable batteries requires the use of organic solvents such as NMP which are toxic and high cost.
- Carbon black (CB) is widely used as conductive agent but causes agglomeration problems.
- Cathode slurries have serious agglomeration problems leading to mechanical properties weakness and shorten shelf life.
- PAA binder is proposed for aqueous processing as it plays a role of dispersant in water-based slurries. But LFP and CB dispersibility in PAA depends on slurries' pH, or polymer structure: linear PAA polymer can adsorb on the particles.

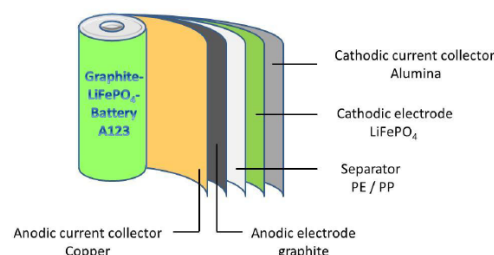


Figure 1. LFP battery composition

Materials & Methods

In this study, two dispersions were studied at various pH conditions (3.0, 6.0, 7.7 and 12).

Dispersed particle	Concentration	PAA supplement
LiFePO_4	10^{-1} vol%	10^{-2} wt%
CB	10^{-3} vol%	$0.5 \cdot 10^{-3}$ wt%

These preparations were dispersed in water and analyzed for 12 hours using the Turbiscan Lab equipment.

Reminder on SMLS technique

Turbiscan® technology, based on static multiple light scattering, consists on illuminating a sample with an infrared light source and acquiring backscattered (BS) and transmitted (T) signals over the whole height of the sample. By repeating this measurement over time, the instrument enables to monitor physical stability.

$$BS \text{ and } T = f(\varphi, d, n_p, n_f)$$

The signal is directly linked to the particle's concentration (φ) and size (d) according to the Mie theory, with refractive index of continuous (n_f) and dispersed phase (n_p) being known parameters.

Results

Case 1: LiFePO_4 ($10^{-1}\text{vol}\%$) / PAA ($10^{-2}\text{wt}\%$)

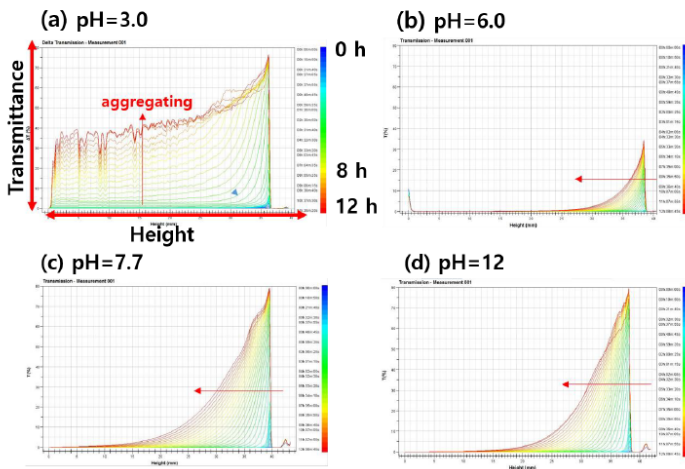


Figure 2 : Transmitted signals T for dispersions of LiFePO_4 at pH=3.0 (a), 6.0 (b), 7.7(c) and 12.0(d).

As shown in Figure 2 (a), at pH=3.0 the dispersion is strongly unstable. We observe a large increase of the transmission T at the top of the sample (right side of the graph) indicating a rapid clarification. In addition, the transmission evolution in the middle of the sample indicates an agglomeration of the particles.

At pH 6.0, 7.7 and 12.0, [Figure 2 (b), (c) and (d)], the dispersions are more stable as we observe a smaller increase of the transmission T . However, a clarification at the top of the sample is still visible which proves that particles are settling.

This clarification zone is the smallest at pH=6.0. This means that particles have a lower settling velocity and are logically smaller in this case thanks to PAA adsorption on LFP avoiding agglomeration.

Case 2: CB ($10^{-3}\text{vol}\%$) / PAA ($0.5 \cdot 10^{-3}\text{vol}\%$)

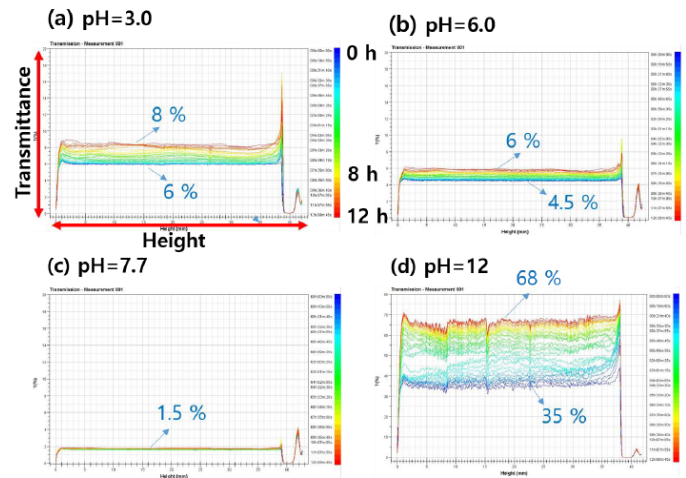


Figure 3. Transmission signals T for dispersions of CB at pH=3.0 (a), 6.0 (b), 7.7(c) and 12.0(d).

In Figure 3 (a), (b) and (c), the transmitted signal levels decrease indicating a better dispersibility and the variation over time is also smaller, with almost constant signal at pH 7.7 indicating that stability increases gradually from pH 3.0 to 7.7.

However, as shown in Figure 3 (d), at pH=12.0, both clarification at the top of the sample and agglomeration is noticeably higher than at pH 7.7. This means that particle dispersibility decreases drastically because PAA does not cover CB and does not inhibit agglomeration.

Dispersibility dependence with pH is different for LiFePO_4 and CB dispersions. In the case first case, at low pH low polymer adsorption results in particle aggregation but at higher pH (6.0, 7.7 and 12), polymer adsorption increases and improves the stability of the dispersion. In the case of CB, the best dispersibility and stability is obtained for pH=7.7 proving that polymer adsorption is optimal for this case. At pH 12, strong negative charge prevents polymer adsorption onto particles leading to a strong destabilization of the dispersion.

CONCLUSION

Thanks to Turbiscan® technology based on Static Multiple Light Scattering (S-MLS) it was possible to evaluate the effect of pH on aqueous battery slurries for LiFePO_4 and CB particles dispersed with PAA polymers. These results have allowed determine optimal pH for polymer adsorption onto particles. This information is capital in order to avoid heterogeneity of battery slurry during production leading to a shorter shelf-life.