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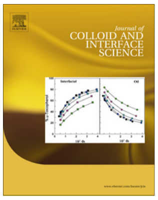

Optimization of multicomponent aqueous suspensions of lithium iron phosphate ($LiFePO_4$) nanoparticles and carbon black for lithium-ion battery cathodes

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ABSTRACT

Addition of polyethyleneimine (PEI) to aqueous $LiFePO_4$ nanoparticle suspensions improves stability and reduces agglomerate size, which is beneficial to lithium-ion battery cathode manufacturing. This research examines the effect of both PEI concentration and molecular weight (MW) on dispersing $LiFePO_4$ and Super P C45 in multicomponent aqueous suspensions. It is demonstrated that the optimal conditions for obtaining stable suspensions with minimal agglomerate size are 1.5 wt% PEI with MW = 2000 g mol^{-1} and 5.0 wt% PEI with MW = 10,000 g mol^{-1} for $LiFePO_4$ and Super P C45, respectively. The mixing sequence also affects rheological properties of these suspensions. It is found that dispersing the $LiFePO_4$ and Super P C45 separately yielded suspensions with superior properties (Newtonian rheological behavior, smaller agglomerate size, improved settling, etc.). In particular, dispersing the $LiFePO_4$ prior to the Super P C45 when making the final multicomponent suspension is found to be beneficial, which was evidenced by higher half-cell discharge capacity.

1. Introduction

Recent interest in widespread commercialization of lithium-ion battery (LIB) technologies for hybrid and electric vehicles requires significantly increased cell manufacturing capability beyond today's levels. As production of these cells is scaled up, it is critical that manufacturing methods are conducted in an environmentally sustainable and economically viable manner.

Current LIB cost is too high, with the cost of materials and associated processing comprising over 80% of the total costs of high power batteries [1,2]. Specifically, cathode raw materials and processing alone may account for up to 70% of cell material cost of lithium-ion battery cathodes [2]. If lower cost materials could be developed and low-cost material processing could be implemented, LIBs would become more affordable [3].

Water is a low-cost, non-hazardous solvent. Replacing N-methylpyrrolidone (NMP), which is the state-of-the-art solvent system for cathode around the world, with water would introduce substantial advantages in economy and environment. NMP is expensive, toxic and produces flammable vapors during electrode manufacturing, which requires expensive explosion proof processing equipment and costly solvent recovery and recycling process. All these add up cost in both raw materials and processing of batteries. An aqueous process is also more environmentally benign because it eliminates the toxic NMP and ecotoxic raw chemicals associated with the production of PVDF, [4,5] in addition to reducing CO_2 emissions during battery manufacturing process [6].

However, transitioning the manufacture of LIB electrodes from an organic process to an aqueous one introduces some disadvantages, due to different polarities of the solvents and surface chemistry of solid components, such as particle agglomeration, slurry stability, viscosity control, wetting of the slurry to the current collector, and adhesion between the slurry and the current collector. Particle agglomeration, which also has significant effect on slurry stability and viscosity control, is caused by the attractive potential generated from van der Waals force dominant between colloidal particles [7]. The inferior wetting of aqueous slurry to the current collector and adhesion between the slurry and the current collector is attributed to high surface tension of the aqueous slurry induced from higher surface tension of water [8].

Advancements have been made in addressing these problems. It was reported in our previous work that the contact angle between $LiFePO_4$ aqueous suspension and Al foil can be reduced from 41.8° to 0° via corona treatment on the Al foil, indicating an improvement

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in wetting of the dispersion to the Al foil [8]. Progress in controlling agglomerate size and stability of the electrode suspensions using a dispersant [7,9–12] and/or water soluble binders [13–18] has also been reported. Li et al. used the anionic dispersant poly (4-styrene sulfonic acid) (PSSA) to improve the dispersion of $LiFePO_4$ composite cathodes [10]. In contrast, our group reported successful implementation of the cationic dispersant polyethyleneimine (PEI) for $LiFePO_4$ aqueous suspensions based on zeta potential results [7]. This addition of PEI improved suspension stability, and it demonstrated Newtonian behavior during rheological measurements. Addition of PEI also reduced the suspension agglomerate size and improved the $LiFePO_4$ performance in half cells [7,19]. Thus, PEI was selected as the dispersant for this optimization study.

Uniform electrode suspension is critical to electrode coating and performance. Most of the previous work [9,10] using a dispersant to improve suspension homogeneity and stability was limited to an evaluation of the concentration effect of the dispersant on active materials only. The effect of dispersing the other major electrode additive (i.e., carbon black) and the molecular weight (MW) effect of dispersants had not been addressed. In this work, the effect of concentration and MW of PEI were optimized for both $LiFePO_4$ and carbon black, respectively, in terms of agglomerate size and suspension stability (rheology).

The order of addition during mixing also plays a critical role in preparing electrode dispersions with respect to electrode performance [20–22], the analysis of which is also limited in the literature. It has been reported that better electrode performance can be obtained by premixing dry particles (active material and carbon black) and adding binder solution and liquid solvent in sequence [20]. Typically, sequences of adding solvent during dispersion preparation affect final rheological properties of suspensions. Lower viscosity and more uniform distribution of electrode components were observed in the final suspensions by adding solvent to solid mixture in a stepwise manner as compared to when the suspension was prepared by adding all solvent in one step [21]. In this study, effect of mixing sequence in preparing electrode suspensions on processing and half-cell performance was discussed in detail. Four mixing sequences were examined to investigate effects on rheological properties of $LiFePO_4$ suspensions and $LiFePO_4$ cathode performance.

2. Materials and methods

As received $LiFePO_4$ (2–3 wt% C coating, P2, d_{50} = 0.5–1.0 μm, Phostech Lithium Inc.), Super P C45 (Timcal) (C45 hereafter), xanthan gum binder (XG hereafter, Nuts Online), and branched PEI (MW = 600, 2000, 10,000, 25,000, and 750,000 g mol^{-1}, Sigma–Aldrich) were used. The molecular structure of branched PEI has been reported in Ref. [19]. C45 and XG were selected as the conductive additive and binder, respectively.

Solutions of PEI with five MWs and five concentrations (0.25–5.0 wt%) were mixed separately with $LiFePO_4$ and then were repeated for C45. The suspensions were prepared by dissolving PEI in deionized (DI) water and mixing for 10 min, followed by dispersing $LiFePO_4$ and C45 into the resulting solutions, and mixing by a high-shear rotar mixer (model 50, Netzsch) for 20 min, respectively. Viscosity of the suspensions was measured at 25 °C by a controlled stress rheometer (AR-G2, TA Instruments). Agglomerate size distribution of the suspensions was measured in water at 25 °C by laser diffraction (Partica LA-950V2, Horiba Scientific). Based on the results of the rheological properties and agglomerate size, optimal PEI in terms of MW and concentration was determined for both $LiFePO_4$ and C45 suspensions.

Four mixing sequences were investigated to prepare $LiFePO_4$ cathode suspensions. The ratio of components in all suspensions was maintained at $LiFePO_4$/C45/XG/H_2O = 100/10/2.5/350 wt fraction. The total mixing time in each sequence was 30 min. In sequence 1 (S1), 1 wt% XG solution was mixed with the selected PEI concentrations and MWs for either $LiFePO_4$ and C45 and the desired amount of DI water for 10 min. $LiFePO_4$ powder was dispersed into the solution above for 10 min followed by dispersing C45 to the resulting suspension for 10 min. Sequence 2 (S2) was similar to S1 except reversing the dispersing sequences of $LiFePO_4$ and C45. For sequence 3 (S3), $LiFePO_4$ and C45 were mixed separately with the desired PEI amount and half of the XG solution for 10 min, respectively. The two suspensions were then combined and mixed for another 10 min. In sequence 4 (S4), both $LiFePO_4$ and C45 were added to the PEI and XG solution simultaneously instead of sequentially (as in S1 and S2) and mixed for 20 min.

$LiFePO_4$ cathodes for half-cell testing were prepared by casting the $LiFePO_4$ suspensions on pretreated Al foil manually using a doctor blade with 100 μm wet thickness. The Al foil was corona treated (Compak 2000, Enercon) at 1.7 J cm^{-2} to increase its surface energy close to the surface tension of water (72.8 mJ m^{-2} at 25 °C) and, thus, achieve better wetting of $LiFePO_4$ suspension [8]. The wet electrodes were dried at 90 °C in a vacuum oven for 3 h. The areal loading of $LiFePO_4$ cathodes was 2.1 mg cm^{-2}.

Half cells were assembled inside an argon filled glove box with $LiFePO_4$ and Li metal foil as the cathode and anode, respectively. Celgard 2325 was used as the separator, and 1.2 M $LiPF_6$ in ethylene carbonate: diethyl carbonate (3/7 wt ratio, Novolyte) was used as the electrolyte. The cells were cycled at 0.2C/−0.2C between 2.5 and 4.2 V with VSP potentiostats (BioLogic) at 25 °C. The C-rate was calculated based on the theoretical capacity of 170 mAh g^{-1}.

3. Results and discussion

3.1. Rheological property and agglomerate size of suspensions

3.1.1. Rheological property and agglomerate size optimization of $LiFePO_4$–H_2O suspensions

Fig. 1 shows the rheological properties of $LiFePO_4$–H_2O suspensions with PEI MW = 600 g mol^{-1} using five concentrations (data for the other MWs are given in Fig. S1). PEI concentration was based on the weight fraction of $LiFePO_4$. There was an initial drop in viscosity with increasing shear rate. The viscosity also slightly decreased with increasing PEI wt%, indicating better dispersion of $LiFePO_4$ (i.e., less agglomeration), which may be attributed to stronger repelling Coulomb forces from adsorbing PEI offsetting attracting van der Waals forces [7]. Another reason for lower viscosity could be more available solvent (water) with increasing PEI wt%. $LiFePO_4$ has an extremely high surface energy (219 mJ m^{-2}) [8], and it is highly hydrophilic. Therefore, water could be captured in the internal voids of the $LiFePO_4$ agglomerates and remains there throughout the electrode processing [20]. A reduced extent of agglomeration could have reduced the amount of entrapped water within $LiFePO_4$ agglomerates, and as a result of the lower measured viscosity, more of the water could have participated in dispersing the $LiFePO_4$.

Additionally, the viscosity decreased with increasing shear rate for these suspensions when the PEI concentration was $\leqslant$0.25 wt%, indicating shear thinning behavior, as compared to the greatly reduced dependence of viscosity on shear rate for those suspensions with a PEI concentration >0.25 wt% (demonstrating Newtonian behavior). This is verified from the plots of shear stress versus shear rate in Fig. 1b), which were fitted with the Herschel–Bulkley (H–B) model. The H–B equation may be utilized in situations where a nonlinear dependence exists of shear stress on shear rate. It is described by the power-law equation and is given as:

$$\begin{cases} \tau = \tau_0 + K\dot{\gamma}^n & \text{if } \tau > \tau_0 \\ \dot{\gamma} = 0 & \text{if } \tau \leq \tau_0 \end{cases} \quad (1)$$