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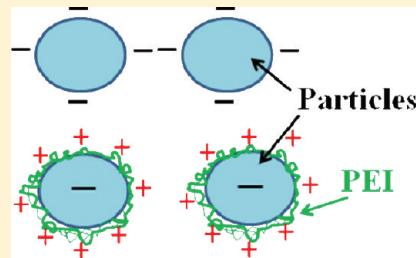
Optimization of LiFePO₄ Nanoparticle Suspensions with Polyethyleneimine for Aqueous Processing

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ABSTRACT: Addition of dispersants to aqueous based lithium-ion battery electrode formulations containing LiFePO₄ is critical to obtaining a stable suspension. The resulting colloidal suspensions enable dramatically improved coating deposition when processing electrodes. This research examines the colloidal chemistry modifications based on polyethyleneimine (PEI) addition and dispersion characterization required to produce high quality electrode formulations and coatings for LiFePO₄ active cathode material. The isoelectric point, a key parameter in characterizing colloidal dispersion stability, of LiFePO₄ and super P C45 were determined to be pH = 4.3 and 3.4, respectively. PEI, a cationic surfactant, was found to be an effective dispersant. It is demonstrated that 1.0 wt % and 0.5 wt % PEI were required to stabilize the LiFePO₄ and super P C45 suspension, respectively. LiFePO₄ cathode suspensions with 1.5 wt % PEI demonstrated the best dispersibility of all components, as evidenced by viscosity and agglomerate size of the suspensions and elemental distribution within dry cathodes. The addition of PEI significantly improved the LiFePO₄ performance.



INTRODUCTION

Rechargeable lithium-ion batteries have received extensive attention in the last two decades and have been used in portable electronic devices such as laptop computers, cellular phones, and personal digital assistants. However, application to electric vehicles and grid energy storage is limited by performance and cost.¹ The main components of battery costs are materials, labor, and overhead with the cost of materials and associated processing making up over 80% of total costs of high power batteries.² Thus, the key to reducing costs of lithium-ion batteries lies in achieving low cost materials and developing low cost material processing,³ which is especially true for the cathode. Cathode materials and processing represent the majority of the total cost of high power batteries.²

LiFePO₄ is a promising cathode material for the next generation of scalable lithium-ion batteries, which is ascribed to low price, good cycle life,⁴ safety,⁵ and low environmental impact (i.e., no toxic elements in the compound). For conventional lithium-ion batteries, the manufacturing process of LiFePO₄ cathodes involves a slurry processing in which LiFePO₄ is mixed with other additives in a solvent. Polyvinylidene fluoride (PVDF) and *N*-methyl-2-pyrrolidone (NMP) are the typical binder and solvent, respectively. If the composite cathodes could be processed through an aqueous system, in which the expensive NMP (>\$2.25/L when purchased in large quantity) is replaced with deionized water (\$0.015/L), the cost would be significantly reduced, and the process for recovery and treatment of NMP would be eliminated. Based on a recent Oak Ridge National Laboratory (ORNL) processing cost study, this approach has a potential to save up to 70% in the electrode processing steps translating to a 12% reduction of the overall battery pack cost.

Additionally, replacing PVDF with xanthan gum⁶ or carboxymethyl cellulose (CMC)⁷ would reduce fluorine content in the electrodes, and the formation of LiF could be suppressed. The overall process would become substantially more environmentally benign; consequently, there is growing interest in fabricating composite cathodes through aqueous processing.⁸ However, replacing NMP with water creates problems with dispersion stability. Particles in water based dispersions can agglomerate due to hydrogen bonding and strong electrostatic forces.⁹ These driving forces are even more problematic for LiFePO₄, since the material is optimized for improved electrochemical performance by making nanoparticles (i.e., larger surface area).

Agglomeration is caused by the interactions between colloidal particles. These interactions include attractive and repulsive potentials, which are generated from van der Waals and Coulomb forces, respectively. Usually, the attractive potential is dominant at greater distances between particles. The stability of the particles depends on the net potential generated between the van der Waals and Coulomb forces. Therefore, to minimize agglomeration, the key is to increase the repulsive potential (i.e., increase the Coulomb force) between particles. The repulsive potential depends on the particle surface charge, and it is measured indirectly. The measurement is known as the zeta potential, and it is mostly dependent on the surface chemistry of colloidal particles.¹⁰ The agglomeration can be mitigated or eliminated by adding a dispersant to the aqueous slurries, and

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there has been some progress in this area.^{8c,g,h,11} Porcher et al.^{8h} chose a nonionic dispersant, Triton X-100, to improve the dispersion of carbon black. Li et al. used the anionic dispersants poly(acrylic acid) (PAA-NH₄)^{8c} and poly(4-styrene sulfonic acid) (PSSA)^{8g} to improve the dispersion of LiCoO₂ and LiFePO₄ composite cathodes, respectively. However, the dispersant effect on processing of the electrodes is rarely discussed.

Our strategy to improve the dispersion of C-coated LiFePO₄ (LiFePO₄ hereafter) suspensions is by a cationic dispersant, polyethylenimine (PEI), which was selected based on the isoelectric point (IEP) of each cathode component, determined by the zeta potential measurement. The zeta potential of each cathode component with and without PEI was determined, and the effect of PEI on the rheological properties of LiFePO₄ suspensions and LiFePO₄ cathode performance was also investigated.

EXPERIMENTAL SECTION

As received LiFePO₄ (2–3 wt % C, P2, Phostech Lithium Inc.), Super P C45 (Timcal) (C45 hereafter), xanthan gum binder (XG hereafter, Nuts Online) and polyethylenimine (PEI) ($M_w = 25\,000\text{ g mol}^{-1}$, Sigma-Aldrich) were used. Super P carbon black is a common carbon black used in lithium-ion batteries. Super P 45 (BET surface area $\sim 45\text{ m}^2/\text{g}$) shows lower surface area compared to Super P 65 (BET surface area $\sim 65\text{ m}^2/\text{g}$), which allows for easier dispersion in water. XG is a cheap, nontoxic binder that has been demonstrated in lithium-ion batteries.⁶

Zeta potential measurements were carried out on LiFePO₄, C45, and XG in dilute aqueous suspensions using electrophoretic light scattering (Zetasizer 3000HS, Malvern Instruments). Dilute suspensions with a solids volume fraction of $\sim 10^{-5}$ were prepared by dispersing the desired amount of powders in KNO₃ (0.001 mol L⁻¹) in distilled water. The suspension pH was adjusted between 2 and 10 using solutions of HNO₃ (1 mol/L) and NH₄OH (1 mol/L), respectively. Dilute suspensions were mixed by magnetic stirring, and pH was measured by a pH meter. Both pH and zeta potential of the dilute suspensions were measured at 25 °C immediately after the suspensions were prepared and after the suspensions were stored for 24 h. A period of 24 h was selected, since it represents a reasonable duration between preparation and processing of electrode suspensions for lithium-ion batteries and it allows adequate time for charge adsorption and desorption on the LiFePO₄ particle surfaces to reach equilibrium. Only the zeta potential results after 24 h stabilization are used in this work, and each data point was averaged from 10 measurements.

The influence of dispersant concentration on viscosity and agglomerate size was investigated for four different suspensions: LiFePO₄ suspensions; C45 suspensions; LiFePO₄ and C45 suspensions; and LiFePO₄, C45, and XG suspensions. 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 media at 25 °C by laser diffraction (Partica LA-950 V2, Horiba Scientific). The first step in preparing the suspensions was to dissolve 10 wt % PEI in deionized (DI) water. The desired amount of PEI solution was mixed with DI water for 2 min followed by mixing with LiFePO₄ or C45 by a high-shear mixer (model 50, Netzsch) for 30 min to obtain a LiFePO₄ or C45 suspension. For LiFePO₄–C45 suspensions, LiFePO₄ was first added to the PEI solution and mixed for 15 min. Then, C45 was added to the suspensions and mixed for another 15 min. For LiFePO₄–C45–XG suspensions, a similar process was used to obtain LiFePO₄–C45 suspensions except the mixing time was reduced to 10 min for each step. Finally, the desired amount of 1 wt % XG solution in DI water was added to the suspension and mixed for 10 min. The ratio of components in all suspensions was maintained at LiFePO₄/C45/XG/H₂O = 100/10/2.5/250 wt fraction.

The suspensions were coated by a custom slot-die coater (Frontier Industrial Technology) on pretreated Al foil and dried in a vacuum oven at 90 °C for 2 h. The Al foil was pretreated by corona discharge (Compak 2000, Enrocon) at 1 kW and 10 ft min⁻¹ to improve its surface energy. The distribution of each component in the composite

LiFePO₄ cathodes was characterized by energy dispersive spectroscopy (EDS) mapping using scanning electron microscopy (SEM) (JEOL 6500 FEG-SEM). The morphology of the dried LiFePO₄ green tapes with and without PEI additions were characterized by scanning electron microscopy (SEM) (JEOL 6500 FEG-SEM).

Half cells were assembled with LiFePO₄ and Li metal as the cathode and anode, respectively, with Celgard 2325 as the separator and 1.2 M LiPF₆ in ethylene carbonate/diethyl carbonate (3/7 wt ratio, Novolyte) as the electrolyte. The cells were cycled at 0.2 C/–0.2 C between 2.5 and 4.2 V with VSP potentiostats (BioLogic) at 25 °C.

RESULTS AND DISCUSSION

Zeta Potential Analysis. Zeta potentials of the LiFePO₄ aqueous cathode suspension are shown in Figure 1 with and without PEI. From Figure 1a, it is seen that the isoelectric point

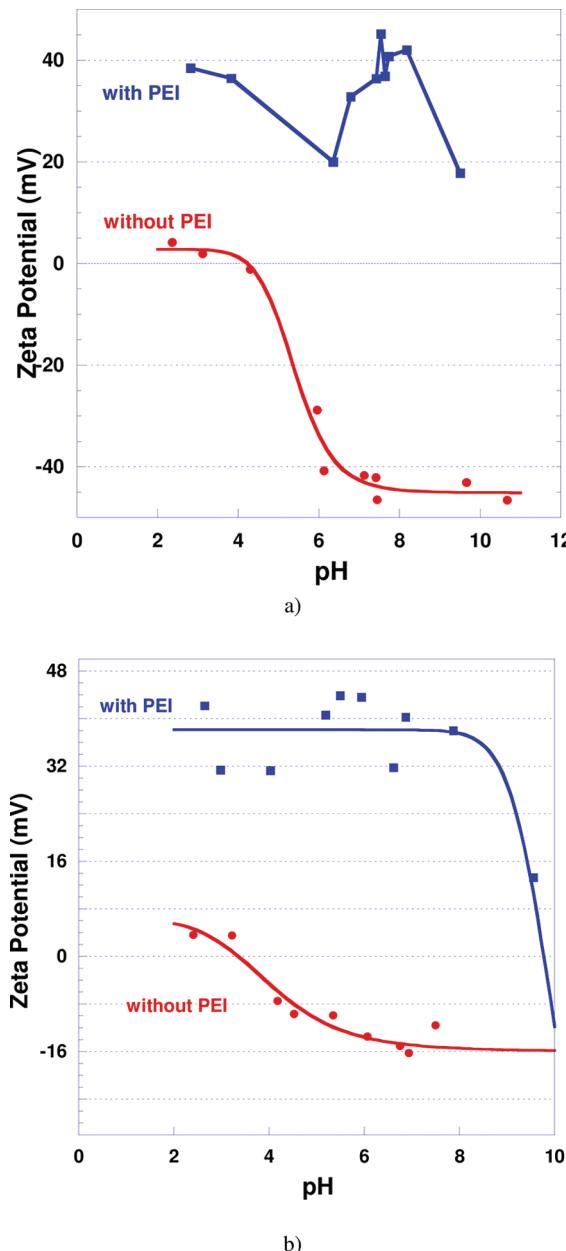


Figure 1. Zeta potential of each component of LiFePO₄ aqueous cathode suspensions with and without PEI. (a) C–LiFePO₄. The presence of PEI changes the charge on C–LiFePO₄ surface to positive; (b) C45, the presence of PEI changes the charge on C45 surface from predominantly negative to positive.

(IEP) of LiFePO₄ was pH = 4.3, the point where the charge on the particle surfaces is zero. It is here that the suspension is in its least stable state with respect to particle agglomeration. The IEP also provides guidance on selection of the type of dispersant (surfactant) required to obtain a stable dispersion. A dispersant is an additive used to control particle separation, which allows for increasing solids loading in a powder suspension and for controlling particle packing during processing.¹² It has been reported that anionic dispersants such as poly(acrylic acid) (PAA)^{7a} and poly(4-styrene sulfonic acid) (PSSA)^{8g} were used in the LiFePO₄ aqueous suspensions. According to Figure 1a, the charge on the surface of the LiFePO₄ particles is negative at pH > 4.3. The appropriate pH for LiFePO₄ suspensions should be close to neutral to avoid corrosion on aluminum current collectors in the subsequent coating processes.

Addition of PEI has been shown to yield a positive charge in aqueous ceramic suspensions at pH < 10¹³ while PAA has been shown to yield a negative charge at pH > 3 due to the protonation. These findings can be extended to our suspensions in that a cationic dispersant, such as PEI, with positive charge should adsorb more easily on LiFePO₄ particles than an anionic dispersant with negative charge. The zeta potentials of LiFePO₄ with PEI dispersant is also shown in Figure 1a, and it is seen that the values changed to positive across the entire pH range indicating PEI successfully adsorbed on the surface of LiFePO₄ particles. Note that in typical zeta potential measurements, solutions are aged 24 h to achieve an equilibrium charge state. The scatter seen in the zeta potentials measured in this study are attributed to nonequilibrium conditions existing at the time of measurement. An experiment to study the effect of longer equilibrium times on the resulting zeta potential values is planned.

In LiFePO₄ aqueous cathode suspensions for lithium-ion battery electrodes, there are two other components required, the C45 conductive carbon black additive and the XG binder (water-soluble). To have maximum efficacy as a dispersant for the LiFePO₄ aqueous cathode suspension, PEI also needs to be efficient in dispersing the C45. Therefore, the zeta potential of C45 was also investigated with and without PEI and is shown in Figure 1b.

According to Figure 1b, the IEP of C45 was found to be pH = 3.4, and the charge on the surface of the C45 particles was negative at pH > 3.4. This data suggests that PEI is an appropriate dispersant for C45 similar to the findings for LiFePO₄. However, this is confirmed by the zeta potential of C45 when PEI dispersant is added (see Figure 1b). The charge on the C45 particle surfaces changed from predominantly negative without PEI to highly positive with PEI. Therefore, it can be concluded that PEI is an appropriate dispersant for both solid components in LiFePO₄ aqueous cathode suspensions.

Suspension Rheological Properties. In order to understand the effect of PEI on aqueous processing of LiFePO₄ cathode suspensions, rheological properties of the suspensions with individual and multiple components were investigated with different PEI concentrations. All PEI concentrations investigated in this work are referenced to the LiFePO₄ weight fraction. Figure 2a, b shows the apparent viscosity and shear stress, respectively, as a function of shear rate for LiFePO₄ suspensions. The viscosity significantly decreased with addition of PEI, and the suspensions also showed shear thinning behavior without PEI (i.e., when viscosity decreases with increasing shear rate). Newtonian or slightly shear thickening (i.e., when viscosity is constant or slightly increases with increasing shear rate) behavior was observed when PEI was added to the suspensions. These

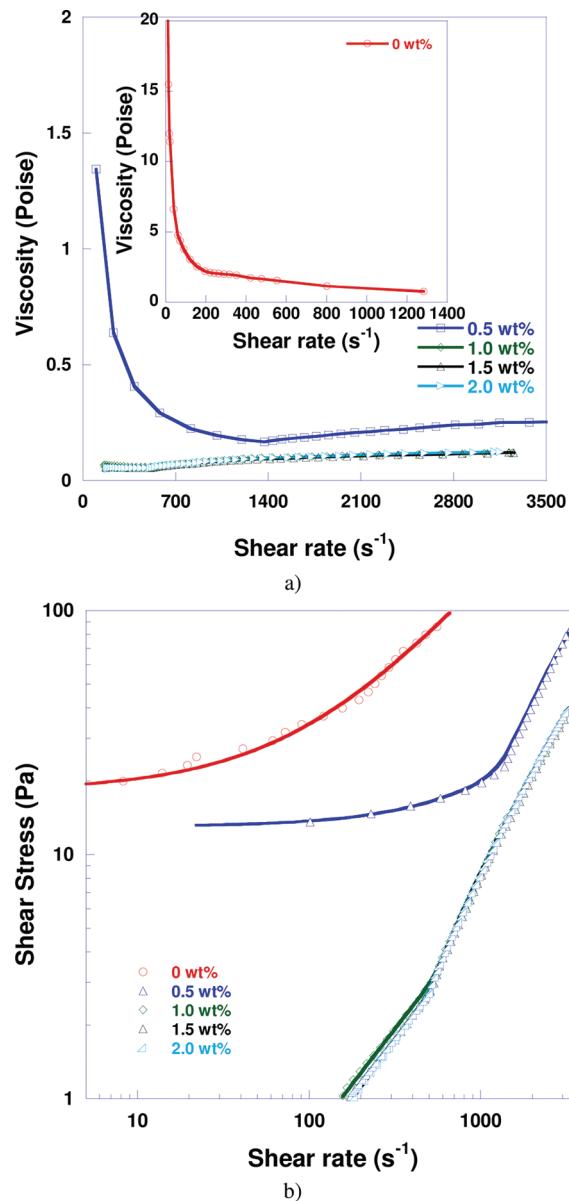


Figure 2. Rheological properties of LiFePO₄ nanoparticle suspensions with various amounts of PEI (a) viscosity vs shear rate and (b) shear stress vs shear rate.

properties were further verified by the shear stress results shown in Figure 2b, which were fitted with the Herschel–Bulkley (H–B) model. The H–B equation is one of the most employed models for situations where a nonlinear dependence exists of shear stress on shear rate. It is described by the power law equation and is stated as the following:

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

where τ , τ_0 , K , $\dot{\gamma}$, and n are the shear stress, yield stress (stress needed to initiate the flow), consistency index, shear rate, and power-law index, respectively. If $n = 1$, this function reduces to the classical Bingham plastic equation. If $\tau_0 = 0$ and $n = 1$, this function describes Newtonian behavior. The LiFePO₄ suspension without PEI showed shear thinning behavior with $n = 0.86$ and $\tau_0 = 18.3$ Pa, as shown in Table 1, which indicates relatively

Table 1. Parameters from the H–B Model for the LiFePO₄ Suspensions

PEI conc	τ_0 (Pa)	n	shear rate (s^{-1})
0 wt %	18.3	0.86	whole range
0.5 wt %	13.1	1.00	<1310
	-12.4	1.14	>1310
1.0 wt %	0.01	0.91	<500
	-2.2	1.15	>500
1.5 wt %	0.04	0.98	<500
	-1.72	1.22	>500
2.0 wt %	0.14	0.98	<500
	-1.434	1.22	>500

strong interaction between agglomerates. In contrast, the addition of 0.5 wt % PEI changed the LiFePO₄ suspension from shear thinning to Bingham plastic with $n = 1.00$ and $\tau_0 = 13.1$ Pa for a shear rate below 1310 s^{-1} and slightly shear thickening with $n = 1.14$ and $\tau_0 = -12.4$ Pa for shear rate above 1310 s^{-1} , respectively. For higher PEI concentrations, the LiFePO₄ suspensions showed Newtonian behavior with $n \approx 1$ and $\tau_0 \approx 0$ Pa at $\dot{\gamma} < 500$ s^{-1} , and slightly shear thickening at $\dot{\gamma} > 500$ s^{-1} , respectively. The decrease in yield stress with increasing PEI concentration indicates that the interaction between the agglomerates was dominated by van der Waals forces for low or zero PEI concentrations. For higher PEI concentrations, such forces were offset and eventually dominated by Coulomb forces, induced by the adsorption of PEI on the LiFePO₄ particles. Thus, the suspensions were stabilized and formed an ordered, layered structure. For further increases in shear rate, the suspensions showed slightly shear thickening behavior, which is ascribed to the order–disorder transition of the ordered, layered structure above a critical shear rate. At this point, the suspensions became unstable and more viscous.¹⁴ The critical shear rate provides important information for suspension processing, and it is demonstrated that 1.0 wt % PEI is enough to stabilize LiFePO₄ in water.

Figure 3 shows the rheological results of the C45 suspensions, and their fitting parameters from the H–B model are listed in Table 2. All of the suspensions showed shear thickening behavior ($n > 1$) at high shear rate. At low shear rate, however, the suspensions with PEI showed Newtonian behavior ($n = 1$) as compared to shear thinning behavior ($n < 1$) for the suspension without PEI. The suspensions with PEI were well-dispersed and stable with the yield stress equal or close to 0 Pa. The shift from Newtonian to shear thickening at high shear rate is also due to the order–disorder transition of the layered structure of C45 particles. Thus, 0.5 wt % PEI is enough to well disperse C45 in water.

Rheological properties of suspensions composed of LiFePO₄–C45 were also measured (Figure 4), and the fitting parameters from the H–B model are listed in Table 3. All of the suspensions except the one with 1.5 wt % PEI showed shear thinning behavior, and the suspensions with 1.0 wt % and 2.0 wt % PEI exhibited quasi-Newtonian behavior with the power-law index close to unity, that is, $n \approx 0.90$. In contrast, the suspension with 1.5 wt % PEI showed shear thickening behavior. From the weight fraction of materials, it could be assumed that 1.5 wt % PEI is enough to disperse the LiFePO₄–C45 suspensions, since the LiFePO₄ and C45 suspensions need 1.0 wt % and 0.5 wt % PEI, respectively, to achieve Newtonian behavior. However, the rheological properties are more complicated and affected by several additional factors,

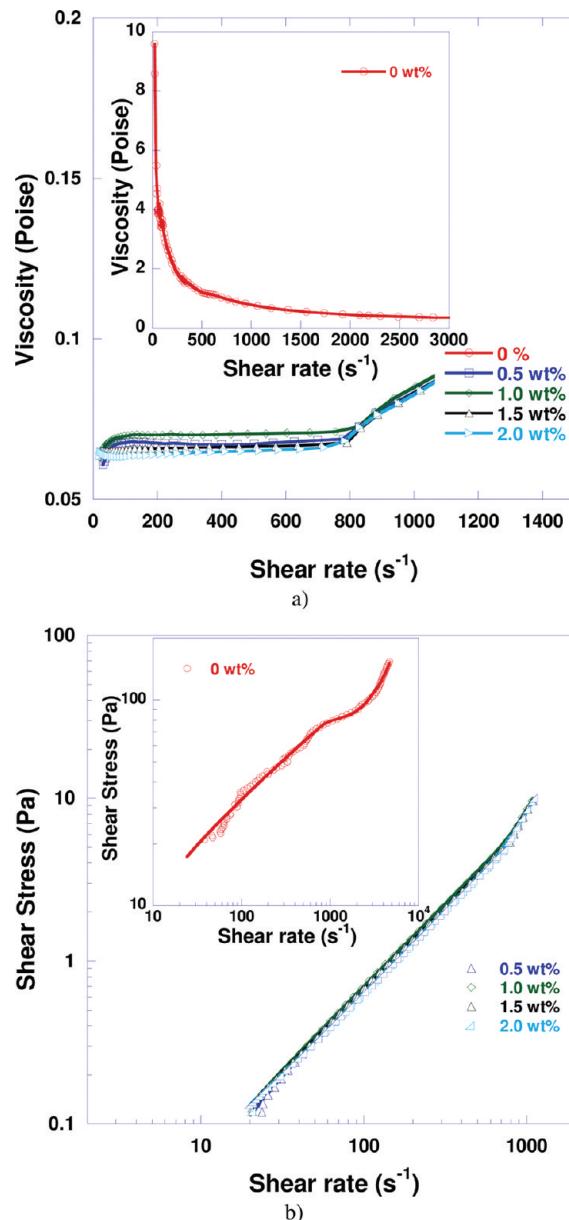
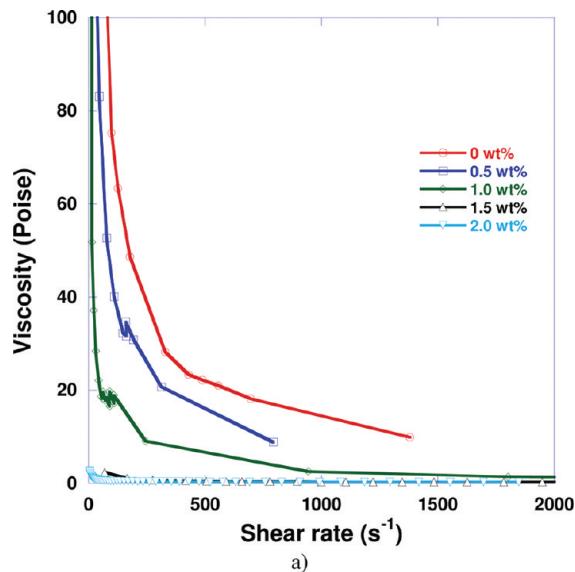


Figure 3. Rheological properties of C45 suspensions with various amounts of PEI (a) viscosity vs shear rate and (b) shear stress vs shear rate.

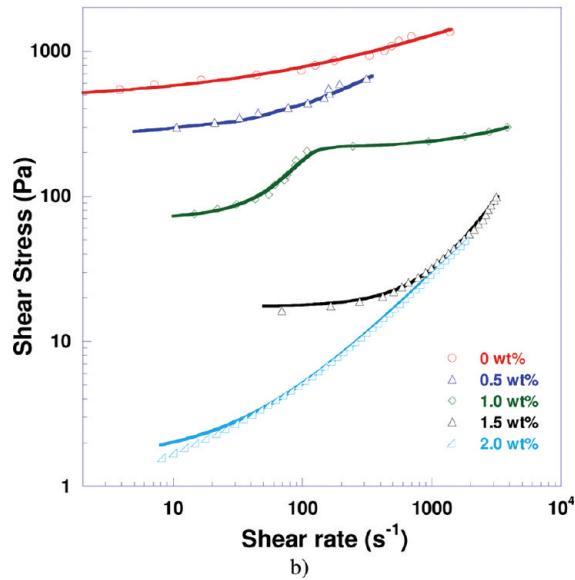
Table 2. Parameters from the H–B Model for the C45 Suspensions

PEI conc	τ_0 (Pa)	n	shear rate (s^{-1})
0 wt %	-6.57	0.35	<820
	77.9	2.36	>820
0.5 wt %	-0.03	0.98	<600
	2.23	2.42	>600
1.0 wt %	-0.01	1.01	<800
	0.10	1.76	>800
1.5 wt %	0.00	1.01	<750
	0.10	1.76	>750
2.0 wt %	0.01	1.03	<750
	0.1	1.75	>750

including weight fraction of materials and mixing method, sequence, time, and so forth. This phenomenon of shear thickening is under investigation and will be discussed in future



a)



b)

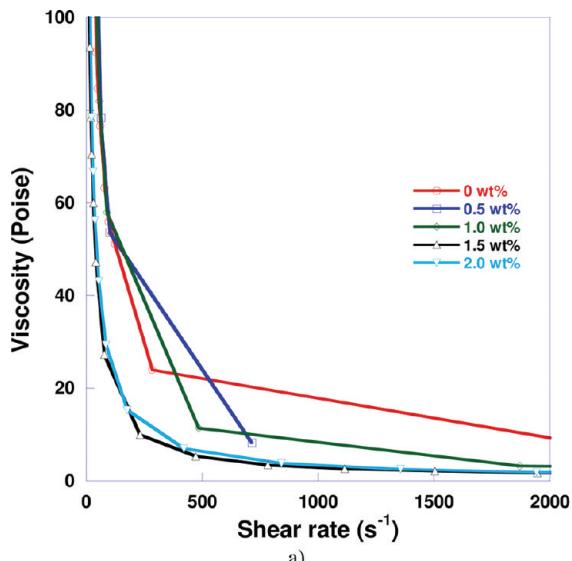
Figure 4. Rheological properties of LiFePO_4 -C45 suspensions with various amounts of PEI (a) viscosity vs shear rate and (b) shear stress vs shear rate.

Table 3. Parameters from the H–B Model for the LiFePO_4 -C45 Suspensions

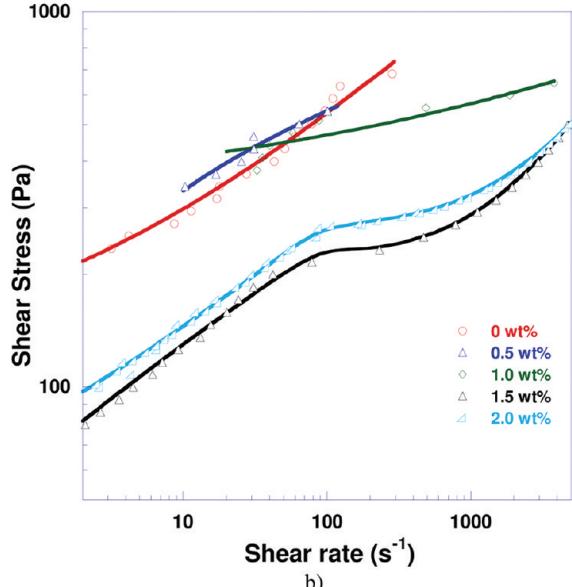
PEI conc	τ_0 (Pa)	n	shear rate (s^{-1})
0 wt %	452.1	0.41	whole range
0.5 wt %	249.7	0.64	whole range
1.0 wt %	71.1	1.68	<100
	214	0.89	>100
1.5 wt %	17.4	1.52	whole range
2.0 wt %	1.57	0.90	whole range

publications. Nevertheless, the decrease in the yield stress confirmed that the interaction between agglomerates decreased with increasing PEI concentration.

Finally, the rheological properties of the LiFePO_4 aqueous cathode suspensions with all components were investigated and are shown in Figure 5. The fitting parameters from the H–B model are listed in Table 4. All of the suspensions with XG binder showed shear thinning behavior, and the addition of XG further reduced their power-law indices compared to the



a)



b)

Figure 5. Rheological properties of LiFePO_4 -C45-XG suspensions with various amounts of PEI (a) viscosity vs shear rate and (b) shear stress vs shear rate.

Table 4. Parameters from the H–B Model for the LiFePO_4 -C45-XG Suspensions

PEI conc	τ_0 (Pa)	n	shear rate (s^{-1})
0 wt %	111.2	0.36	whole range
0.5 wt %	-3244	0.03	whole range
1.0 wt %	314.9	0.22	whole range
1.5 wt %	-22.3	0.24	<150
	216.3	0.92	>150
2.0 wt %	28.5	0.33	<100
	260	0.87	>100

LiFePO_4 -C45 suspensions. The addition of XG also increased the yield stress significantly, which is ascribed to the interlinking of particles by XG molecules. The suspensions with 1.5 wt % and 2.0 wt % PEI exhibited the lowest yield stresses and closest power-law indices to unity resulting in the highest quality suspensions.

PEI Effect on Suspension Agglomerate Size. Figure 6 shows the d_{50} values of the agglomerates for all suspensions.

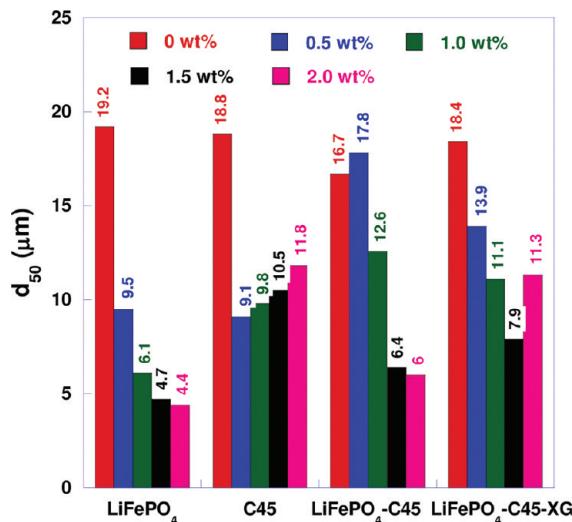


Figure 6. d_{50} of the suspensions as a function of PEI. Note: The PEI concentration is based on LiFePO₄. It will be 10 times if based on C45, since LiFePO₄/C45 = 10/1 wt.

The d_{50} decreased with increasing PEI concentration for the LiFePO₄ suspensions demonstrating that better dispersion was obtained at higher PEI concentrations. Based on the rheological results in the Suspension Rheological Properties section, the suspensions exhibited Newtonian behavior with 1.0 wt % or more PEI. However, the distance between agglomerates might not have been large enough at 1.0 wt % PEI, and multiple agglomerates might have acted as one large agglomerate during the size distribution measurement. Smaller d_{50} with higher PEI concentration translates to a higher quality dispersion, either smaller agglomerate size or greater distance between agglomerates. In contrast, the C45 suspensions exhibited Newtonian behavior with 0.5 wt % to 2.0 wt % PEI; however, the corresponding d_{50} increased with increasing PEI concentration. This finding indicates PEI reached saturated adsorption on C45 particles at 0.5 wt %, and at higher PEI concentrations, additional PEI molecules in the suspensions bridged with other PEI molecules adsorbed on C45 particles forming larger agglomerates. For the LiFePO₄-C45 suspensions, the d_{50} values decreased with increasing PEI and were relatively constant with 1.5 wt % and 2.0 wt % PEI indicating the optimum PEI concentration was 1.5 wt %. A minimum d_{50} was observed in the LiFePO₄-C45-XG suspensions with 1.5 wt % PEI demonstrating saturated adsorption of PEI on the agglomerate surfaces was reached.

Morphology of Coated LiFePO₄ Cathodes. Homogeneity of each component distributed in coated LiFePO₄ cathodes (coatings made with the suspensions containing all components) was qualitatively characterized by energy dispersive spectroscopy (EDS) mapping (Figure 7). The cathodes without PEI showed a rough surface with lots of voids (Figure 7a), and the components were not distributed uniformly (i.e., carbon rich spots). In contrast, the cathodes with PEI exhibited a smoother surface and were much denser. There were still some carbon rich spots in the cathode with 0.5 wt % (Figure 7b). However, it was observed that the components were well-dispersed for the cathodes with 1.0 wt % PEI or above. This finding verifies the addition of PEI improves the suspension quality and the resulting dispersion of each component in the coated LiFePO₄ cathodes.

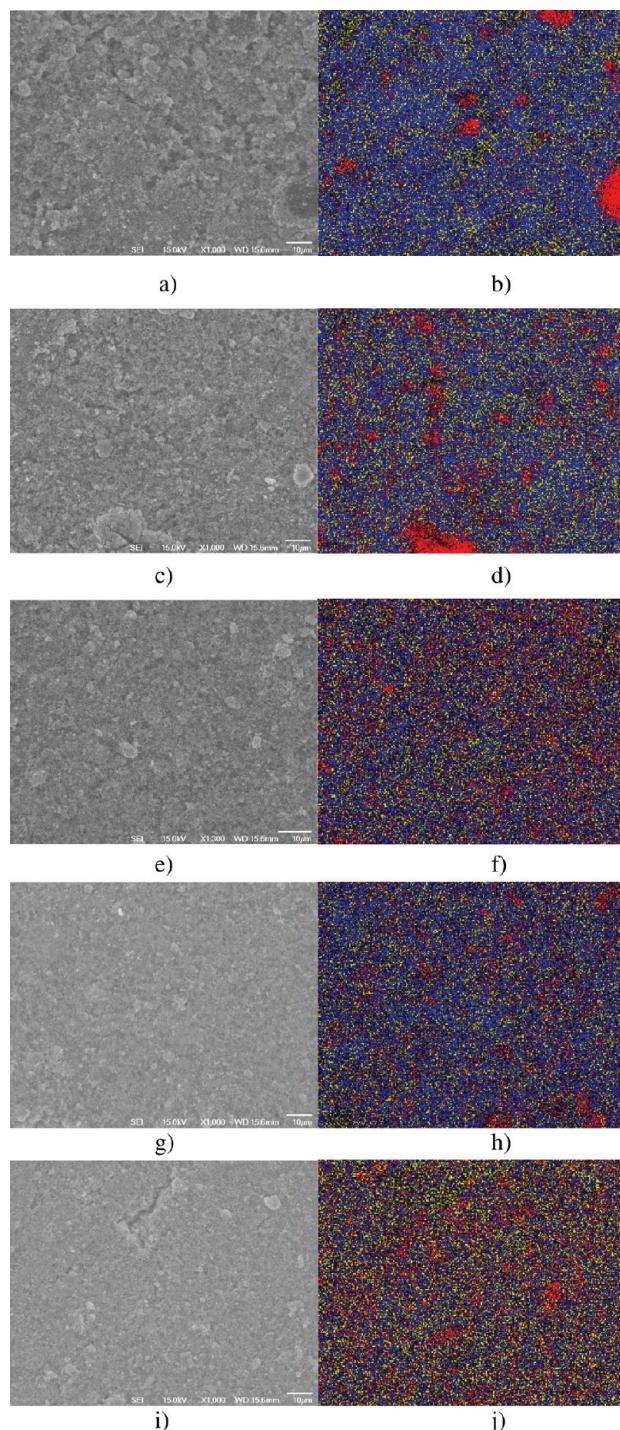


Figure 7. SEM observation of LiFePO₄ composite cathodes. The intense red, blue, and yellow represent C, P, and Fe, respectively. (a, b) without PEI; (c, d) 0.5 wt % PEI; (e, f) 1.0 wt % PEI; (g, h) 1.5 wt % PEI; and (i, j) 2.0 wt % PEI.

Performance of LiFePO₄ Cathodes. It is common that the capacity of LiFePO₄ cathodes increases in the first couple cycles, which is attributed to the reintercalation of the deintercalated lithium via air and water exposure.¹⁵ Figure 8 shows the voltage profiles of LiFePO₄ cathodes at the fifth cycle at which the deintercalated lithium was reintercalated. The addition of PEI significantly improved the LiFePO₄ cathode performance. The LiFePO₄ with 2.0 wt % PEI exhibited the best capacity (~165 mAh/g). Furthermore, the plateaus were much

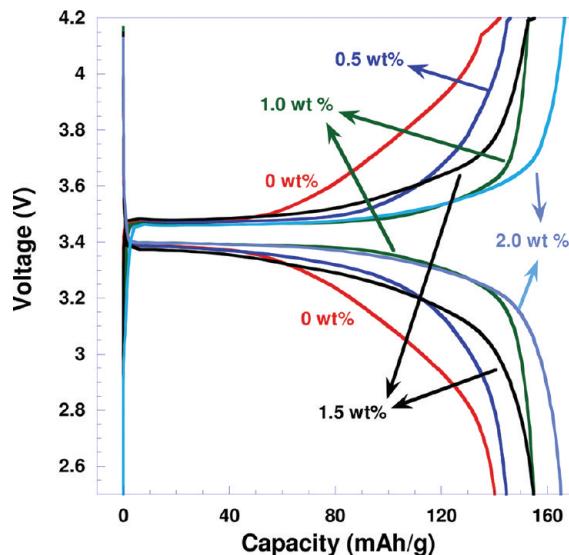


Figure 8. Voltage profile versus capacity curves at 0.2 C / -0.2 C and 25 °C confirming the addition of PEI improved the LiFePO₄ cathode performance.

broader with PEI, and the polarization was much smaller. This could be attributed to the smaller agglomerate size and more homogeneous distribution of cathode components, which favors lithium diffusion inside the LiFePO₄ agglomerates and the interfacial charge transfer.

CONCLUSIONS

It has been demonstrated that PEI is highly effective in dispersing the components of LiFePO₄ cathodes for lithium-ion batteries. The effect of PEI concentration on suspensions with individual or multiple cathode components were studied. Concentrations of 1.0 wt % and 0.5 wt % PEI are required to stabilize LiFePO₄ and C45, respectively, in water. For the suspensions with all components, 1.0 wt % PEI showed shear thinning behavior, whereas 2.0 wt % PEI exhibited close to Newtonian behavior. The addition of PEI increased the dispersion homogeneity of LiFePO₄ cathode components and reduced the agglomerate size. These results provide guidance in suspension processing and electrode coating of LiFePO₄ composite cathodes for lithium-ion batteries through aqueous processing. The addition of PEI dramatically improved the LiFePO₄ cathode performance.

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Notes

The authors declare no competing financial interest.

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