1. Introduction

Lithium iron phosphate (LiFePO₄) has received great attention as a promising alternative cathode material for rechargeable lithium ion batteries due to its high energy density, low cost, safety, and chemical stability. In particular, since the recall of several million notebook computer batteries due to the potential risk of explosion of lithium ion batteries, the safety issues of lithium ion batteries have become the center of public attention. This has resulted in an acceleration of the commercial use of LiFePO₄ due to its intrinsic safety and chemical stability as cathode materials, compared to the layered rock salt oxides LiCoO₂ and LiNiO₂ and the spinel LiMn₂O₄.

Generally, positive electrode films for commercial lithium ion batteries are prepared by a tape casting process using a non-aqueous slurry whose suspending media consists of organic solvents. However, since organic solvents are typically toxic and flammable, various attempts have been made to switch from non-aqueous- to aqueous-based systems. For example, Lee et al. and Porcher et al. investigated the stability of LiFePO₄ in an aqueous medium from the standpoint of dispersion and electrochemistry, respectively. Guerfi et al. investigated the effect of a new water-soluble elastomer as a new binder for the LiFePO₄ cathode materials in a lithium ion battery. So far, few investigations have examined the correlation between dispersion properties and electrochemical properties in an aqueous medium. It is reported that the formation of an agglomeration caused by poor dispersion leads to degraded power properties at high C, because the agglomeration acts as a resistance. According to Lee et al., the addition of poly(acrylic acid) (PAA) significantly decreases the apparent viscosity of the LiFePO₄ paste, which results from the improved dispersion properties of LiFePO₄. However, direct evidence showing a correlation between the dispersion properties and rate properties was not provided.

In the present investigation, we investigated the effect of PAA on the dispersion properties of C/LiFe-
PO₄ and its resulting high power properties of C/LiFePO₄ positive electrodes for applications in lithium-ion batteries. A stable, aqueous-based C/LiFePO₄ slurry was prepared with a combination of two organic additives, namely carboxymethyl cellulose (CMC) and water-soluble elastomer binder (WSB), with and without PAA. CMC is used primarily as a thickening agent to prevent the C/LiFePO₄ particles from settling and segregating during processing. WSB and PAA were introduced as a binder and a dispersant for C/LiFePO₄, respectively. The effect of incorporating PAA into the suspension was characterized by measuring the electrokinetic response, particle size distribution and shear rheological behavior for the formulated suspension. Finally, the rate behavior of the coin cell fabricated by our formulated suspension was evaluated as a function of C rate.

2. Experimental

Carbon-coated LiFePO₄ (C/LiFePO₄) was obtained from a commercial source (Samsung SDI Co. Ltd., Korea) and had an average particle diameter of 300 – 500 nm. Dynamic light scattering measurements showed that the d50 was 382 nm and the polydispersity index was 0.243. The carbon content, as stated by the manufacturer, was about 2 wt%. The BET surface area was measured using N₂ and found to be 13 m²g⁻¹. Carbon black was used as a conducting agent. CMC (Daicel Co. Ltd., Japan) with an average molecular mass of 330,000 and a degree of substitution of DS=1.28 was used as a thickening agent. PAA (50% solution in water) with an average Mr of 5,000 was obtained from Polysciences, Inc. (Warrington, PA, USA). A water-soluble elastomer binder (Zeon Corp., Japan) was used as the elastomeric binder. Unless otherwise stated, concentrations of organic additives are expressed on a mass basis relative to the C/LiFePO₄ phase.

All suspensions were prepared with filtered de-ionized water (18MΩ resistance) and ultrasonicated for three min using a high-intensity submersible horn (5000A, Shimadzu Corp., Kyoto, Japan). The final pH values for all of the suspensions were between 8.9 and 9.3 and were not independently controlled.

For electrokinetic measurements, suspensions containing a C/LiFePO₄ mass fraction of 5% were prepared in deionized water, with and without PAA, and subsequently treated ultrasonically for 3 min. The treated suspensions were then allowed to equilibrate at room temperature for 12 h with magnetic stirring, after which they were ultrasonicated for an additional 3 min. The required amounts of CMC and WSB were then added, and the suspensions were equilibrated for an additional 12 h. Electrokinetic curves were determined using an electroacoustic analyzer (Model ESA-9800, Matec Applied Sciences, Hopkinton, MA, USA) operating nominally at 1 MHz.

Particle size distribution was measured at 25 ± 1°C using a Nano ZS (Malvern Instrument, Malvern, UK). The mass fractions of C/LiFePO₄ and carbon black were 40% and 0.83%, respectively. Sample preparation followed the same procedure previously described for ESA measurements. The required amount of carbon black was incorporated into the suspension after addition of CMC and WSB. Due to the high viscosity, the C/LiFePO₄ paste containing C/LiFePO₄ and carbon black was diluted by 5 wt%.

The rheological behavior of the C/LiFePO₄ paste containing C/LiFePO₄ and carbon black was determined at 25 ± 1°C using a controlled-stress rheometer (MCR501, Paar Physica, Stuttgart, Germany) with a concentric cylinder geometry (DG 27). The mass fractions of C/LiFePO₄ and carbon black were 40% and 0.83%, respectively. Sample preparation followed the same procedure previously described for ESA measurements. The required amount of carbon black was incorporated into the suspension after addition of CMC and WSB. The apparent viscosities of the C/LiFePO₄ suspensions were measured as a function of the ascending shear rate.

The discharge specific capacity of the fabricated coin cell was evaluated as a function of the number of cycles. The electrolyte was 1.3M LiPF₆ in a 3:7 volume mixture of ethylene carbonate (EC) and diethyl carbonate (DEC).

3. Results and Discussion

Fig. 1 shows the pH-dependent electrokinetic behavior of C/LiFePO₄ particulates as a function of used organic additives, CMC, WSB and PAA. The electrokinetic curves show that C/LiFePO₄ particles containing CMC and WSB with and without PAA exhibited a negative surface potential across the measured pH range. This resulted from the presence of a carboxyl functional group in the adsorbed layer of the CMC. In our previous investigation, we reported that the native carbon-coated C/LiFePO₄ particles showed a net negative charge across the normal pH range which implied that the bare surface of the C/LiFePO₄ particle rather than the carbon-coated area of the C/LiFePO₄ was mainly responsible for this negative surface potential. CMC and PAA ion-
ize with increasing pH to form a negatively charged macromolecule due to dissociation of carboxylic acid groups. Therefore, the adsorption of an organic additive on C/LiFePO₄ is mainly driven through hydrophobic interactions because of mutually repulsive electrostatic forces between the native C/LiFePO₄ and organic additives. However, in the acidic region, the adsorption of organic additives on C/LiFePO₄ can be driven by either hydrogen bonding or hydrophobic interaction due to the low degree of dissociation of organic additives. Furthermore, partial substitution of CMC with PAA resulted in a significantly decreased dynamic mobility. We investigated the effect of PAA on the development of surface potential for graphite and C/LiFePO₄ and reported that the addition of PAA does not contribute to further development of electrokinetic potential (surface charge) of particulates. Therefore, it is possible to infer that the reduced amount of CMC is responsible for the reduced dynamic mobility of nanosized LiFePO₄.

Particle size distributions of 5wt%-diluted C/LiFePO₄ paste containing CMC and WSB with and without PAA were measured in order to evaluate the agglomeration state of C/LiFePO₄, and the results are shown in Fig. 2. It is found that the addition of PAA shifted particle size distribution to lower value, which is attributed to the improved dispersion properties of C/LiFePO₄ paste. These improved dispersion properties of C/LiFePO₄ originate from the enhanced particle-particle interaction. It has been reported that PAA has a stronger adsorption affinity with hydrophobic surfaces than does CMC, and under basic conditions, PAA has a more favorable conformation for dispersion of particles due to electrostatic repulsive forces.

Rheological behaviors of C/LiFePO₄ paste containing CMC and WSB with and without PAA were characterized, and the results are shown in Fig. 3. All pastes show shear thinning behaviors, showing linear dependence of the viscosity on the shear rate. Shear thinning of the concentrated suspensions is known to appear because of structure formation (i.e., aggregation) and structure breakdown (because of the applied shear), with a concurrent increase in overall viscosity. Furthermore, it was observed that the apparent viscosity of the paste decreased with an increase in the concentration of CMC. This was inconsistent with the previous results because CMC plays a role as a thickening agent, so the increase of CMC concentration results in an increase of the apparent viscosity of the paste. The decreased apparent viscosity of the paste may be attributed to the improvement of the dispersion properties of the C/LiFePO₄ or the effect of WSB. This issue will be addressed in future investigations. It was also noticeable that the addition of PAA significantly decreased the viscosity of the C/LiFePO₄ paste, which resulted from the improvement of dispersion properties of
This is well-consistent with the results for particle size distribution (Fig. 2). Therefore, it is clear that the addition of PAA contributes to the improvement of dispersion properties of C/LiFePO₄ through a steric stabilization.

The rate behaviors of the prepared C/LiFePO₄ positive electrodes were evaluated and are shown in Fig. 4. It was found that the specific discharge capacity of the C/LiFePO₄ electrode containing PAA was not much different from that without PAA at 0.1C, showing about 160 mAh/g. However, at 20C, the electrode with PAA showed a specific discharge capacity that was about seven times higher than that without PAA. This is because the agglomeration of the solid phase resulted in an increase in the resistance of the agglomerated material, which decreased the conductivity of the active materials. This was consistent with the rheological behavior of the C/LiFePO₄ pastes.
4. Conclusion

The dispersion properties of aqueous-based C/LiFePO$_4$ particulates and the resulting electrochemical behaviors were investigated. It was found that the incorporation of PAA resulted in a significant decrease in the viscosity of the C/LiFePO$_4$ paste as well as shift of particle size distribution to lower value. This indicated that the dispersion properties of C/LiFePO$_4$ particles were improved through steric interparticle forces. From the electrochemical performance, the electrode with PAA exhibited a specific discharge capacity about seven times higher than that without PAA at a high C-rate and 20C.

Acknowledgement

This work is the outcome of a Manpower Development Program for Energy & Resources supported by the Ministry of Knowledge and Economy (MIKE).

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