Application of a Polyacrylate Latex to a Lithium Iron Phosphate Cathode as a Binder Material

Mi Tian †, Yanchunxiao Qi † and Eun-Suok Oh *

School of Chemical Engineering, University of Ulsan, 93 Daehak-ro, Nam-gu, Ulsan 44610, Korea; tianmi86@ulsan.ac.kr (M.T.); chunxiao0428@mail.ulsan.ac.kr (Y.Q.)
* Correspondence: esoh1@ulsan.ac.kr; Tel.: +82-52-259-2783
† Equally contributed to this work.

Abstract: In the manufacturing process of lithium-ion batteries, the current organic solvent-based processes will inevitably be replaced with eco-friendly water-based processes. For this purpose, the current organic-soluble binder should be replaced with a water-soluble or water-dispersed binder. In this study, a new polyacrylate latex dispersed in water was successfully applied as a binder of lithium-ion battery cathodes for the first time. One of the biggest advantages of the polyacrylate binder is that it is electrochemically stable at the working voltage of typical cathodes, unlike a conventional water-dispersed styrene-butadiene binder. This implies that the water-dispersed polyacrylate has no limitations for the usage of a cathodic binder. The performance of the polyacrylate binder for lithium iron phosphate cathodes was compared with those of a conventional organic-based polyvinylidene fluoride binder as well as a water-dispersed styrene-butadiene binder. The polyacrylate binder exhibited an electrochemical performance that was comparable to that of an existing styrene-butadiene binder and much better than that of the polyvinylidene fluoride binder. This superior performance of the polyacrylate binder is attributed to the point-to-point bonding mechanism of an emulsified binder, which leads to a strong adhesion strength as well as the low electrical and charge transfer resistances of the cathodes.

Keywords: polyacrylate latex; emulsified water-based binder; lithium iron phosphate cathode; lithium-ion battery

1. Introduction

In recent years, lithium-ion batteries (LIBs) have been used in an extended range of applications, from small portable devices to electric vehicles and energy storage systems [1–4]. There are several imperative issues for LIBs: prolonged cycle stability, high energy and rate capability, low cost, safety, and an environmentally friendly manufacturing process. To cope with these issues, all components of LIB electrodes should be optimized according to the particular application. The electrodes are normally composed of active materials as a major component, as well as a conducting agent and a polymeric binder as minor inactive components [5]. Lithium transition metal oxides containing cobalt, nickel, or manganese have been widely studied over the last few decades [6–11]. However, cobalt and nickel are less common, carcinogenic, mutagenic, and reprotoxic metals, which should be avoided as much as possible in future LIB manufacturing [12,13]. Hence, LiFePO₄ (LFP), which contains abundant and environmentally friendly iron, has attracted the attention of many researchers and industries [14–19]. LFP is also known for its high thermal stability, with appreciable capacity (170 mAh g⁻¹), and its good long-term cycle stability [20].

Beyond the active materials, a polymeric binder is also an indispensable element in LIBs that plays a important role in maintaining the electrical network integrity of the electrode, though it is inactive in electrochemical reactions [21–24]. As a conventional binder for the cathode, polyvinylidene fluoride (PVdF) has typically been used due to its excellent chemical stability [25–27]. However, PVdF should be used in the form of a
solution with a toxic organic solvent, N-methylpyrrolidone (NMP), during the preparation of the electrode slurry [28–30]. This certainly causes difficulties in electrode manufacturing and increases manufacturing costs [31]. Therefore, there have been intensive studies on water-based binders, including styrene-butadiene rubber (SBR), carboxymethyl cellulose (CMC), sodium alginate, polyacrylic acid, polyvinylpyrrolidone, etc. [32–36]. Of these, SBR is the most common water-based binder because of its good flexibility, strong binding force, and high heat resistance [37,38]. In particular, SBR combined with CMC is widely applied in commercial graphite anodes [38–40]. However, SBR is oxidized when a voltage exceeding 4.2 V is applied to LiCoO$_2$ cathodes, because unsaturated C=C double bonds in the butadiene chains of SBR are unstable at such a high voltage [41]. This is one of the reasons to limit the implementation of a water-based SBR binder on LIB cathodes.

A polymeric binder as an inactive component should be stable in anodic and cathodic environments. This is an essential factor in constructing a potential water-based binder that has good electrochemical stability in a wide voltage window when applied to a LIB cathode. In this study, a new water-based polyacrylate latex (PAL) binder will be applied to commercial LFP cathodes for the first time, although polyacrylates such as neutralized polyacrylic acid were used as binders for graphite and silicon graphite anodes [42,43]. Moreover, this binder be compared to typical SBR and PVdF binders in terms of electrochemical stability. In addition, comprehensive electrochemical tests of the LFP cathodes produced by the new binder or the two typical binders will be performed and discussed in detail.

2. Materials and Methods

The water-based electrode slurry was composed of 90 wt% of active material LFP (Advanced Lithium Electrochemistry Co. Ltd, Taoyuan City, Taiwan), 5 wt% of super-p (SP, Alfa Aesar, Tewksbury, MA, USA), 2 wt% of thickener CMC (Daicel Fine Chem Ltd., Osaka, Japan), and 3 wt% of water-based binders PAL or SBR (Zeon Corporation, Tokyo, Japan). PAL (Eco chemical Co. Ltd., Ulsan, Korea) is a type of polyacrylate manufactured from emulsion polymerization; due to the policy of the company, the detailed components of the PAL are not available. The organic-based electrode slurry was composed of LFP, SP, and PVdF (90:5:5 wt.%), and NMP was used as solvent. The slurry was mixed in a planetary ball mill and casted on aluminum foil. The water-based and organic-based electrodes were dried in a convection oven at 60 ºC and 120 ºC for 30 min, respectively. Next, the electrodes were dried again in a vacuum oven at 70 ºC overnight. The mass loading of electrodes was 11.9 ± 0.4 mg cm$^{-2}$. Using the working electrodes, CR2032 coin-half cells were assembled with polypropylene separator film, a lithium chip as a counter electrode, and 1 M LiPF$_6$ in 1:1:1 ethylene carbonate:dimethyl carbonate:ethyl methyl carbonate by volume (Panaxetec Co., Busan, Korea) as electrolyte.

Meanwhile, the electrodes composed of the binder and SP alone were also manufactured to investigate the electrochemical stability of the binder at high voltage. The weight ratios of PAL/CMC:SP, SBR/CMC:SP, and PVdF:SP were 1/1:10, 1/1:10, and 3:7, respectively. These electrodes were also assembled to HS-3E flat (Hohsen Corp., Osaka, Japan) cells with the same counter, separator, and electrolyte as above.

Using the same ways described in our previous study [44], various characteristics of the binder and electrode were examined: the particle sizes of SBR and PAL latex, the adhesion strength of the electrode, and the electrode resistances. Cyclic voltammetry (CV) testing to assess the electrochemical stability of the electrode was performed in the voltage range from 2.0 to 4.5 V, with 10 mV s$^{-1}$ for HS-3E flat cells and 0.25 mV s$^{-1}$ for CR2032 cells using a potentiostat. The electrochemical impedance spectroscopy (EIS) test was performed in the frequency range from 10$^6$ Hz to 10$^{-2}$ Hz at the direct current potential of E = 3.5 V. Long-term cycling and rate capability tests were conducted between 2.5 V and 4.0 V with a CC/CCV charge mood and a CC discharge mood. For long-term cycling tests, the cells were charged/discharged at 0.1 C for the first 3 cycles and at 1 C for the next 100 cycles. The cells were charged/discharged with a variety of currents, ranging from 0.1 C to 10 C.
3. Results and Discussion

First, the electrochemical stability of the binder was investigated through the CV of HS-3E flat cells, and the result is shown in Figure 1. During the 3 cycles within 2.0~4.5 V, the oxidation peaks appear at voltages approximately above 4.2 V only in the SBR electrode, although the peak intensity decreases as the cycle proceeds. However, there is no corresponding reduction peak in the cathodic scan to 2.0 V, indicating that the oxidation of SBR is irreversible. These findings are consistent with those of the previous study. Yabuuchi et al. [41] reported that the unsaturated C=C of butadiene chains in SBR was oxidized at voltages above 4.2 V. By contrast, no distinguishable oxidation peaks exist in the CV curves of the PAL and PVdF electrodes, other than typical electrochemical double layer characteristics [44]. Therefore, there is no doubt that PAL is as electrochemically stable as PVdF within the cathodic working voltage. The slight current increases in the PAL and PVdF electrodes during the anodic scan near 4.5 V are attributable to the electrochemical decomposition of electrolytes. From this simple CV result, the new water-based PAL can be applied as a cathodic binder, at least over LFP electrodes, unlike the SBR binder.

Figure 1. Cyclic voltammetry (CV) of the binder electrodes. The binder electrodes are composed of styrene-butadiene rubber (SBR), polyacrylate latex (PAL), or polyvinylidene fluoride (PVdF) with excess amounts of super-p (SP) conducting agent.

In addition to the environmentally friendly characteristic of water-based latex binders, another outstanding benefit of the latex binders is the use of less binder than in a typical organic-soluble PVdF binder. Because the binder is an electrochemically inactive component of electrodes, its content should be minimized as much as possible. Unlike the PVdF binder of the surface contact mechanism, water-based emulsified binders such as SBR or PAL enter into contact with the active material through the point-to-point binding mechanism, with its fine polymer particles [45]. The fine particles of the water-based emulsified binder can help maintain the electrode integrity with a smaller amount than PVdF, ultimately leading to an increase in capacity, although it remains ambiguous how small particles should optimally be for LIB electrodes. As shown in Figure 2, the average size of PAL particles is around 182 nm, whereas that of SBR particles is approximately 104 nm. The particle size can be easily controlled by modifying the emulsion polymerization techniques and components, such as the temperature and reaction time of the polymerization, the amount of surfactant, initiator, pH stabilizer, etc.; this is out of the scope of this study.
The most important properties of electrodes in terms of binder are their adhesion and electrical resistance. Electrode adhesion was first examined via a mechanical peel test of the electrode, and the result is shown in Figure 3a. No meaningful peel strength was observed for the LFP electrode containing a PVdF binder. Meanwhile, the LFP electrodes containing emulsified PAL and SBR binders showed approximate peel strengths of 15.8 N cm\(^{-1}\) and 25.1 N cm\(^{-1}\), respectively. However, as displayed in Figure 3a, the peel strength of the LFP/SBR electrode was not as stable as that of the LFP/PAL electrode during the test. This implies that the PAL binder disperses in the electrode better than the SBR binder. This is also confirmed by the pictures in Figure 3b that show the dispersion of SP in the binder latices. Due to the hydrophobic nature of carbonaceous SP, SP is hardly dispersed in water. Compared to the dispersion of SP in SBR latex, SP is relatively well dispersed in the PAL latex. This must be attributed to the functional groups in acrylate, such as carboxylate, which can easily interact with the functional groups on SP as impurities. The uniform dispersion of the binder can avoid the aggregation of the active material and SP, which is advantageous for the electrochemical performance of electrodes.

The electrode resistances are measured using 46 multipoint probes connected to a measurement system. The system allows for the electrical resistances of an electrode to be measured without requiring the geometric correction factors caused by typical four-point probe systems. As listed in Table 1, the LFP/PAL electrode has the smallest surface and volume resistivities of the three LFP electrodes, and it also has a slightly higher interface resistance than the LFP/SBR electrode. In particular, compared to a commercial PVdF binder, the PAL binder decreases the volume resistivity of the LFP electrode from 12.2 to 7.27 Ω cm, which corresponds to a decrease of 40.4%. Though the relatively lower adhesion of the LFP/PAL leads to a slightly larger resistance assigned to the interface between the electrode and the current collector than that of the LFP/SBR electrode, the PAL binder is clearly favorable for producing an LFP electrode possessing lower electrical resistance due to its good dispersion in the electrode.
Figure 3. (a) 180° peel strength of LiFePO$_4$ (LFP) electrodes containing PAL, SBR, or PVdF binder. (b) Dispersion of SP in PAL and SBR latices.

Table 1. Surface and volume resistivities and interface resistance of the LFP electrodes.

| Electrode | Composite Thickness (µm) | Composite Surface Resistivity (Ohm cm$^2$) | Interface Resistance (Ohm cm$^2$) | Composite Volume Resistivity (Ohm cm) |
|-----------|--------------------------|-------------------------------------------|-----------------------------------|--------------------------------------|
| PAL       | 16.4                     | $1.19 \times 10^{-2}$                     | 2.93                              | 7.27                                 |
| SBR       | 16.9                     | $1.85 \times 10^{-2}$                     | 1.85                              | 7.59                                 |
| PVdF      | 18.5                     | $2.75 \times 10^{-2}$                     | 8.91                              | 12.20                                |

The electrochemical characteristics of the LFP electrodes were examined using CV and EIS experiments, and the results are depicted in Figure 4. The LFP electrodes containing a PAL or SBR binder show clear and strong oxidation peaks at 3.5 V and symmetrical reduction peaks at 3.3 V; these are respectively assigned to the redox reaction of Fe$^{2+}$/Fe$^{3+}$ in LFP. In both binders, the potential gaps of the peaks are almost the same, at nearly 200 mV. By contrast, the redox peaks of the LFP/PVdF electrode are relatively sluggish, and their potential gap is approximately 800 mV, which is much larger than those of the LFP/PAL and LFP/SBR electrodes. This implies that the polarization resistance of the LFP electrode is decreased when a water-based PAL or SBR binder is used instead of a commercial PVdF binder. This may be why the point-to-point contact of PAL and SBR provides more free paths for the movement of Li$^+$ in the LFP electrode. Further evidence for this point comes from the EIS analysis of the electrodes after four times of cycling. The results are shown in Figure 4b. The size of the semicircle represents the charge transfer resistance for electrochemical reactions occurring at the interface between the electrode and the electrolyte [46]. Meanwhile, the straight line at the low frequency provides information on the Warburg resistance related to the ion diffusion in the electrode [45]. It is obvious from the figure that the charge transfer resistances of the LFP composed of PAL (18.4 Ω) and SBR (21.5 Ω) latex binders are much smaller than that of the PVdF binder (457.5 Ω). In addition, the PAL electrode has a steeper slope than the SBR electrode at low frequency, demonstrating a faster ion diffusion. Overall, the reduced charge transfer resistance and improved ion diffusion achieved with the use of the PAL binder may benefit the electrochemical performance of the LFP electrode.
Finally, Figure 5 shows the electrochemical performance of the LFP electrodes with respect to the long-term cycle and rate-capability. The electrodes containing a PAL or SBR binder show excellent long-term cycling stability with the discharge capacities of 142 mAh g\(^{-1}\) for LFP/PAL and 136 mAh g\(^{-1}\) for LFP/SBR after 100 cycles. By contrast, the LFP/PVdF electrode suffers from severe capacity fading, such that the capacity retention is only 7.1% at the 100th cycle. In addition, the PVdF electrode shows serious unstable coulombic efficiency, whereas the others have superior stable coulombic efficiencies, above 96%. This is consistent with the results of high-rate tests showing that the cells are charged and discharged at various current densities: 0.1 C, 0.2 C, 0.5 C, 1.0 C, 2.0 C, 5.0 C, and 10.0 C. At each current, eight cycles are repeated, and then the current returns to 0.1 C to check the electrode recovery. As shown in Figure 5b, the PVdF electrode shows low capacities even at low currents of 0.1 C and 0.2 C, as well as nearly zero capacity above 0.5 C. This might be caused by the network bonding mechanism of the PVdF binder, i.e., the weak adhesion strength, high electrical resistances, and significant charge transfer resistance caused by the PVdF binder. By contrast, the PAL and SBR electrodes show a good rate performance with a capacity retention relatively higher than 50%, even at 10 C. In addition, the electrodes fully restore their capacities when 0.1 C is given to the electrodes from 10 C, implying that they do not suffer any physical damage with such high current charge/discharge cycles. Further, it is clear from Figure 5c,d, showing the charge-discharge profiles at different current densities, that the LFP/PAL electrode has more stable voltage profiles than the LFP/SBR electrode.

In summary, the PAL binder is a promising water-based binder candidate for an LFP cathode, due to its excellent electrochemical stability at high voltages, pleasant dispersion in slurry, satisfactory adhesive strength, and small surface and volume resistances.
Figure 5. Electrochemical performance of the electrodes containing different binders: (a) long-term cycling, (b) rate capability. (c,d) are the voltage-capacity profiles of the electrodes at various currents.

4. Conclusions

Similarly to the commercial SBR binder for LIB anodes, the new PAL binder makes the manufacturing process of LIB cathodes eco-friendly, because it is dispersed in water as an emulsion state. However, unlike the SBR binder, the PAL binder is electrochemically stable at such a high working voltage of LIB cathode, due to the lack of a carbon-carbon double bond in the main chain of PAL. The CV result confirms that the PAL has a good electrochemical stability, up to 4.5 V, just like organic-based PVdF binder. In addition, when compared to the PVdF binder used for normal cathodes, there are several advantages originating from the point-to-point bonding mechanism of the PAL binder. The LFP cathode manufactured by the PAL binder has a stronger adhesion strength, lower electrical resistances, and better charge transfer characteristics than that manufactured by the PVdF binder. Consequently, the LFP cathode containing the PAL binder could achieve an excellent specific discharge capacity of 155 mAh g$^{-1}$ with a high capacity retention of 91.5% after 100 cycles at 1.0 C. Even the specific discharge capacity remains at more than 50% when the charge/discharge current density increases up to 10 C. These are much
better than the corresponding values for the LFP cathode composed of the conventional PVdF binder.

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