A novel and efficient water-based composite binder for LiCoO₂ cathodes in lithium-ion batteries

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Abstract

The dispersion, adhesion strength, electrical, and electrochemical properties of LiCoO₂ cathodes in lithium-ion batteries with the addition of a new composite binder composed of two acrylic emulsions, poly(butyl acrylate)-based (PBA) and polyacrylonitrile-based (PA) latex in a ratio of 3:7, were evaluated. PBA binder has a low-glass transition temperature of 10 °C, which can improve the flexibility of the electrode. This new composite binder has a very good binding ability as same as the typical organic solvent-based binder, poly(vinylidene fluoride). The dispersions of the water-based cathode slurries with the composite binder were measured by analyzing the viscosity and sedimentation behaviors. The results show that the new composite binder can well disperse the LiCoO₂. Moreover, using the new composite binder could greatly improve the rate capabilities and the cycle stability of water-based LiCoO₂ cathodes.

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1. Introduction

Lithium cobalt oxide (LiCoO₂) is the most widely used cathode active material in the lithium-ion battery industry due to its high energy density and good cycling-life performance [1]. The LiCoO₂ cathode is generally composed of LiCoO₂ powder, a conductive additive, and a polymer binder. These compositions need to be homogeneously mixed into the solvent in the initial process [2–4]. According to the type of solvent used, the as-prepared suspension can be classified into two categories—a water-based (aqueous) system or an organic solvent-based (non-aqueous) system [5]. For environmental consistency and cost considerations, the water-based system has attracted increasing attention [6–8].

From our previous work [6–8], we found that using the styrene–butadiene rubber (SBR) as a water-based binder mixed with sodium carboxymethyl cellulose (SCMC) as a thickening agent yielded a good conductivity of LiCoO₂ electrodes. However, the LiCoO₂ electrodes did not have sufficient adhesion strength on the aluminum foil, which is used as the current collector in the cathodes. Inversely, the addition with polyacrylonitrile (PA)-based binder, shown in Fig. 1a, gave the electrodes better adhesion properties but decreased their conductivity. However, in the addition with PA-based binder, the adhesion strength of the water-based LiCoO₂ electrodes is, on average, 96 g cm⁻¹, which is still much weaker than that of the organic-based electrodes having an average of 120 g cm⁻¹ [9]. The weaker adhesion of water-based electrodes may be due to the less homogeneous distribution of the binder inside the electrode tape, i.e. most binder is accumulated on the top side of the electrode tape and the bottom side which is contacted with the current collector is binder deficient, because the water-based slurry always needs a longer time to be dried than the organic-based one [10,11]. Thus a binder having higher binding ability than the SBR + SCMC and PA-based binder is required. Without
respectively, by mixing 64.75 g (68.0 wt.%) LiCoO₂ powder and PA-based binder in a ratio of 3:7, were used in order to compare binder in a ratio of 3:7, and (d) PBA-based binder mixed with SCMC in a ratio of 6:4, (c) SBR mixed with PA-based binder. Note that the contents of all additives were based upon the LiCoO₂ powder. The slurries were de-agglomerated and mixed by ball milling with Y₂O₃-stabilized ZrO₂ media for 2–3 days at room temperature. The viscosity of the slurries at a shear rate of 1000 s⁻¹ was measured using a concentric cylinder viscometer (AR1000, TA Instruments Ltd., UK).

The slurries prepared from the above compositions were cast on one side of an aluminum (Al) foil by using a roller coater, and the final thickness of the positive electrode sheets after drying and pressing were approximately 90 μm and 68 μm, respectively. The surface resistance of each LiCoO₂ sheet was measured by a two-point resistance test using a MCP-TESTER FP analyzer. Electrochemical performance was evaluated by assembling cathode-limited 2016 lithium coin cells. LiCoO₂ was used for the cathode. A lithium metal foil electrode was used as the anode. A separator (Celgard 2320) was placed between the cathode and the anode. The electrolyte was 1.0 M lithium hexafluorophosphate (LiPF₆, Tomiyama Pure Chemical) in EC:PC:DEC (3:2:5 in volume) mixed solvents. The cells were charged at a constant current at 0.2 C to 4.2 V and discharged at 0.2 C, 1 C, and 3 C to 2.75 V.

3. Results and discussion

Fig. 2 compares the effect of the additions of different binders, i.e. (a) PA-based binder, (b) SBR + SCMC (6:4), (c) SBR + PA-based binder (3:7), and (d) PBA-based binder + PA-based binder (3:7), on the surface resistance and adhesion strength of as-prepared LiCoO₂ electrode sheets. Among the above binders, both (a) and (b) are the commonly used binders for the water-based cathodes and anodes of lithium-ion batteries [6–8,12,13]. From our previous work [6–8], we found that the electrode with the addition of binder (a) has better adhesion properties than that of binder (b), but it also has higher surface resistance. In order to take advantage of the desirable properties of both binders, i.e. higher adhesion strength from binder (a) and lower surface resistance from binder (b), a composite binder (c) composed of PA-based latex and SBR in a ratio of 3:7 was used. The ratio of 3:7 is the best ratio for the electrical and adhesion properties that we have tested. The substance PA-based latex is a high-viscose binder, thus it can also work as the thickening

![Fig. 1. Chemical structure of the composite binders: (a) polyacrylonitrile (PA) and (b) poly(butyl acrylate) (PBA).](image131x702 to 270x773)

![Fig. 2. The surface resistance and adhesion strength of LiCoO₂ electrodes with different binders.](image361x122 to 577x283)
The average value of the surface resistance is 239 \frac{\Omega}{\text{cm}^2} -1 and the adhesion strength of the electrodes. In order to create a desirable binder, it was proposed to mingle an aqueous emulsion of PBA-based binder that has low \( T_g \) and has good binding ability for general ceramic powders [14,15] with the PA-based latex in an arbitrary ratio of 3:7. From the result shown in Fig. 2, it is obvious that the new composite binder has a higher capacity after 30 charge/discharge cycles. Based on the above results, it is evident that mingling PA-based binder with the PBA-based latex benefits the binding efficiency and has a higher capacity after 30 charge/discharge cycles. In order to further investigate the effect of PBA-based binder on the electrochemical property of the LiCoO\(_2\) cathode, the C-rate performances at 0.2 C, 1 C, and 3 C for the LiCoO\(_2\) half-cells with additions of binder (a) and composite binder (d) were measured and compared, respectively, as shown in Fig. 5. At any discharge rate, the results clearly show that the cell with composite binder (d) has a significant effect on improving the cell stability. Even at the discharge rate of 3 C, the capacity of the cell with binder (d) is still much higher than that of the cell with binder (a) discharged at 1 C. This result agrees well with the measurements of surface resistance and adhesion strength, i.e., great advances in the properties of adhesion strength and surface resistance result in excellent performance of the rate capability. Beside, the cycle-life of the above two LiCoO\(_2\) half-cells were also compared, as shown in Fig. 6. It shows that the cell with binder (d) is more electrochemically stable and has a higher capacity after 30 charge/discharge cycles. Based on the above results, it is evident that mingling PA-based latex with the PBA-based binder benefits the binding efficiency of PA-based latex, yielding better adhesion strength and thus the electronic conductivity, C-rate capability and cycle-life stability of LiCoO\(_2\) electrodes. It should be noted that the ratio of PA-based latex, yielding better adhesion strength and thus the electronic conductivity, C-rate capability and cycle-life stability of LiCoO\(_2\) electrodes. It should be noted that the ratio
Fig. 4. The colloidal stability of 20 wt.% aqueous PBA-based binder suspensions with a respective addition of 10 wt.% powder of LiCoO$_2$ and KS6 during different time periods of (a) 1 min and (b) 3 days.

Fig. 5. Discharge curve at various discharge rates for LiCoO$_2$/Li half-cells prepared with respective additions of PA-based binder and PA-based binder + PBA-based binder.

of PBA-based binder to PA-based latex is only 3/7 and the total binder content in the electrode is still low compared to the organic-processed cathodes. Thus, it can be expected that the adhesion strength, electrical, and electrochemical properties may be further improved as PBA-based binder ratio or the total binder content is reasonably increased, without destroying the dispersion of slurries.

Fig. 6. Cycling stability of LiCoO$_2$/Li half-cells prepared with respective additions of PA-based binder and PA-based binder + PBA-based binder.

4. Conclusions

Based on the results of this work, we conclude that the proposed composite binder composed of the PA- and PBA-based latex is an efficient binder for improving the adhesion strength, electrical, and electrochemical properties of the water-based LiCoO$_2$ cathode in lithium-ion batteries. From the
standpoint of LiCoO$_2$, adhesion to the aluminum foil used as the current collector in the cathode, the proposed composite binder is a great deal more efficient than the reported water-based binder, PA-based latex or SBR + SCMC, and has similar binding ability as the organic-based binder, PVDF. The experimental results of dispersion show that PBA-based binder aggregates with the KS6 powder, but disperses the LiCoO$_2$ powder. Fortunately, the LiCoO$_2$ is the major component in the cathode slurries; thus the dispersion qualities of the slurries were dominated by the interactions between PBA-based binder and the LiCoO$_2$. Due to the high binding capability of the proposed binder, further improvement in adhesion strength, electrical, and electrochemical properties can be expected as PBA-based binder content of the composite binder or the total binder content is reasonably increased.

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References
