

Short communication

## A novel and efficient water-based composite binder for LiCoO<sub>2</sub> cathodes in lithium-ion batteries

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Received 22 June 2007; accepted 31 July 2007

Available online 9 August 2007

### Abstract

The dispersion, adhesion strength, electrical, and electrochemical properties of LiCoO<sub>2</sub> 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 LiCoO<sub>2</sub>. Moreover, using the new composite binder could greatly improve the rate capabilities and the cycle stability of water-based LiCoO<sub>2</sub> cathodes.

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**Keywords:** Lithium-ion batteries; LiCoO<sub>2</sub>; Cathode; Polyacrylonitrile; Poly(butyl acrylate)

### 1. Introduction

Lithium cobalt oxide (LiCoO<sub>2</sub>) 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 LiCoO<sub>2</sub> cathode is generally composed of LiCoO<sub>2</sub> 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 LiCoO<sub>2</sub> electrodes. However, the LiCoO<sub>2</sub> 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 LiCoO<sub>2</sub> electrodes is, on average, 96 g cm<sup>-1</sup>, which is still much weaker than that of the organic-based electrodes having an average of 120 g cm<sup>-1</sup> [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

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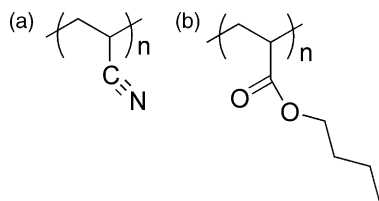


Fig. 1. Chemical structure of the composite binders: (a) polyacrylonitrile (PA) and (b) poly(butyl acrylate) (PBA).

sufficient adhesion strength, the cast electrode sheet will easily peel off from the aluminum foil during the cutting or pressing process, and it can be expected that the resulting sheets will have apparent structural fractures that are harmful to electrode conductivities and cell performance.

In this investigation, we introduce a new aqueous composite binder composed of PA-based and poly(butyl acrylate) (PBA)-based emulsion, Fig. 1, that has a low-glass transition temperature ( $T_g$ ) around 10 °C. This improves the adhesion, the electrical, and electrochemical properties of LiCoO<sub>2</sub> electrodes. The results were also compared to the electrodes with additions of other binders, such as SBR + SCMC, PA-based, and PBA-based + SBR binder. Furthermore, the effect of interactions between the binder and the powders of LiCoO<sub>2</sub> and the conducting additive, KS6, on the dispersion properties of as-prepared slurries were also studied.

## 2. Experimental

The cathode active material used in this study was a high-purity lithium cobalt oxide powder (LiCoO<sub>2</sub>) (L106, LICO, Taiwan). The powder had a median size of 8.0 μm with a standard deviation of 0.45 μm measured by the light scattering (LS-230, Coulter Counter, USA) method. A synthetic graphite Timrex KS6 (Timcal A + G Sins, Switzerland) was used as a conductive agent. Polyacrylonitrile (PA)-based latex (LA132, Indigo, China), styrene–butadiene rubber (SBR, Asahi Kasei Corporation, Japan), and poly(butyl acrylate) (PBA)-based latex, (B1050 Duramax™, Rohm and Haas, USA) are in the form of aqueous emulsions of 15 wt.% with a viscosity of 5000–6000 mPa s at 40 °C, 48 wt.% with a viscosity of 130 mPa s at 25 °C, and 49 wt.% with a viscosity of 100–1000 mPa s at 23 °C, respectively. Sodium carboxymethyl cellulose (SCMC, Aldrich, USA) was used as a thickening agent for the SBR with an average molecular weight of 250,000 g/mol and a substitution degree (DS) of 1.2. De-ionized water was used as a solvent in this study.

Four binders, namely, (a) PA-based binder, (b) SBR mixed with SCMC in a ratio of 6:4, (c) SBR mixed with PA-based binder in a ratio of 3:7, and (d) PBA-based binder mixed with PA-based binder in a ratio of 3:7, were used in order to compare their binding efficiencies.

Cathode slurries containing various binders were prepared, respectively, by mixing 64.75 g (68.0 wt.%) LiCoO<sub>2</sub> powder with additives of 4.20 g (6.1 wt.%) graphite and 1.05 g (1.6 wt.%) binder. Note that the contents of all additives were based upon the LiCoO<sub>2</sub> powder. The slurries were de-agglomerated and mixed

by ball milling with Y<sub>2</sub>O<sub>3</sub>-stabilized ZrO<sub>2</sub> media for 2–3 days at room temperature. The viscosity of the slurries at a shear rate of 1000 s<sup>-1</sup> 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 LiCoO<sub>2</sub> 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. LiCoO<sub>2</sub> 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 (LiPF<sub>6</sub>, 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 LiCoO<sub>2</sub> 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

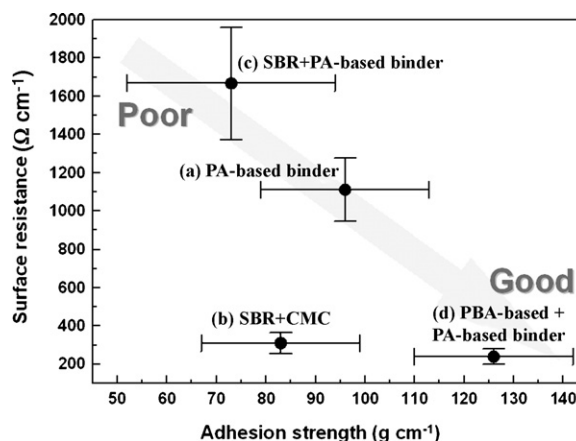


Fig. 2. The surface resistance and adhesion strength of LiCoO<sub>2</sub> electrodes with different binders.

agent for the low-viscose SBR. In Fig. 2, it is clearly seen that the electrode sheet with the addition of composite binder (c), unexpectedly, has the poorest conductivities and adhesions. The reason is not clear yet, but the increased surface resistance might be due to the decreasing adhesion strength of the electrode tape caused from the partial replacement of PA-based latex by SBR. 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 great 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 (d) displays significant improvement in increasing both the conductivity and the adhesion strength of the electrodes. The average value of the surface resistance is  $239 \Omega \text{ cm}^{-1}$  and the adhesion strength is  $126 \text{ g cm}^{-1}$ . The adhesion strength has reached the quality of organic-based cathode electrodes that have an average of  $120 \text{ g cm}^{-1}$  [9]. By comparing the results of using either composite binder (c) or (d), it is obvious that the PBA-based binder is a more efficient binder and compatible with PA-based latex. In addition, the PBA-based binder is an aqueous emulsion consisting of  $0.05\text{--}0.5 \mu\text{m}$  diameter acrylic polymer particles dispersed in water; thus it has very low viscosity and adjusts the high viscosity of PA-based latex. Mingling these two compatible binders, PA-based and PBA-based binder, yields an appropriate viscosity for the slurry casting, as shown in Fig. 3.

Fig. 3 shows the viscosities and equilibrium pH values of as-prepared cathode slurries as a function of PBA-based binder content of binder (d). It shows the slurry with the addition of only PA-based binder having the highest viscosity; the viscosity decreases with increasing PBA-based binder content until 60 wt.% and then increases inversely. When the PBA-based binder content is higher than 80 wt.%, the aqueous slurries start to heavily aggregate and become inhomogeneous and highly viscose. This result demonstrates that there may be some interactions taking place between PBA-based binder and the powders because PA-based latex would not cause the powders to aggregate, which was tested and confirmed by our previous work

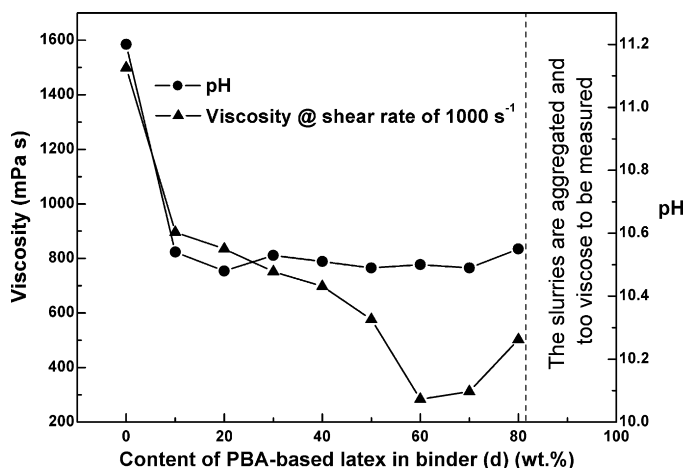


Fig. 3. The viscosity and equilibrium pH of the aqueous  $\text{LiCoO}_2$  slurry as a function of the PBA-based binder content in the PBA- and PA-based binder.

[6,7]. In order to identify which of the powders interacts with the PBA-based binder to cause the slurry to aggregate and become inhomogeneous, two aqueous suspensions containing 20 wt.% PBA-based binder with respective additions of 10 wt.%  $\text{LiCoO}_2$  and KS6 powder were prepared and their dispersion stabilities were recorded. Fig. 4 shows the aqueous suspensions of  $\text{LiCoO}_2$  and KS6 in the presence of PBA-based binder after different time periods, respectively. In the initial state after 1 min, the  $\text{LiCoO}_2$  powder was homogeneously distributed in the suspension as shown in Fig. 4(a). After 3 days, some of the  $\text{LiCoO}_2$  powder settled to the bottom of the vial, and some was well suspended in the upper supernatant and thus the suspension remained cloudy. From the above sedimentation results of  $\text{LiCoO}_2$ , it is known that PBA-based binder is efficient in dispersing the  $\text{LiCoO}_2$  powder. Apparently different from the result of  $\text{LiCoO}_2$ , the KS6 powder was not homogeneously distributed but segregated from PBA-based binder solution in the initial state. After 3 days, segregations became more obvious. This result demonstrates that the KS6 powder was incompatible with PBA-based binder. Fortunately,  $\text{LiCoO}_2$  is the major component of the cathode slurry. Therefore, the dispersion quality of the suspension is dominated by the interactions between PBA-based binder and  $\text{LiCoO}_2$ . The results shown in Figs. 2–4 reveal that the addition of low-viscose PBA-based binder lowers the viscosity of slurries and increases the adhesion and electrical properties of electrode sheets; however, when the addition of PBA-based binder becomes too high, it obviously interacts with the KS6 powder and results in an adverse effect on the slurry dispersions. Furthermore, the equilibrium of the pH values in the slurries was also measured. After the addition of PBA-based binder, all slurries have pH values of lower than 10.6. An aqueous slurry would corrode the aluminum substrate if the slurry is too basic, i.e.  $\text{pH} > 11$  [8]. Thus the addition of PBA-based binder has the advantage of protecting the aluminum substrate from corrosion.

In order to further investigate the effect of PBA-based binder on the electrochemical property of the  $\text{LiCoO}_2$  cathode, the C-rate performances at 0.2 C, 1 C, and 3 C for the  $\text{LiCoO}_2$  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 rate capabilities. 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 results in excellent performance of the rate capability. Besides, the cycle-life of the above two  $\text{LiCoO}_2$  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  $\text{LiCoO}_2$  electrodes. It should be noted that the ratio

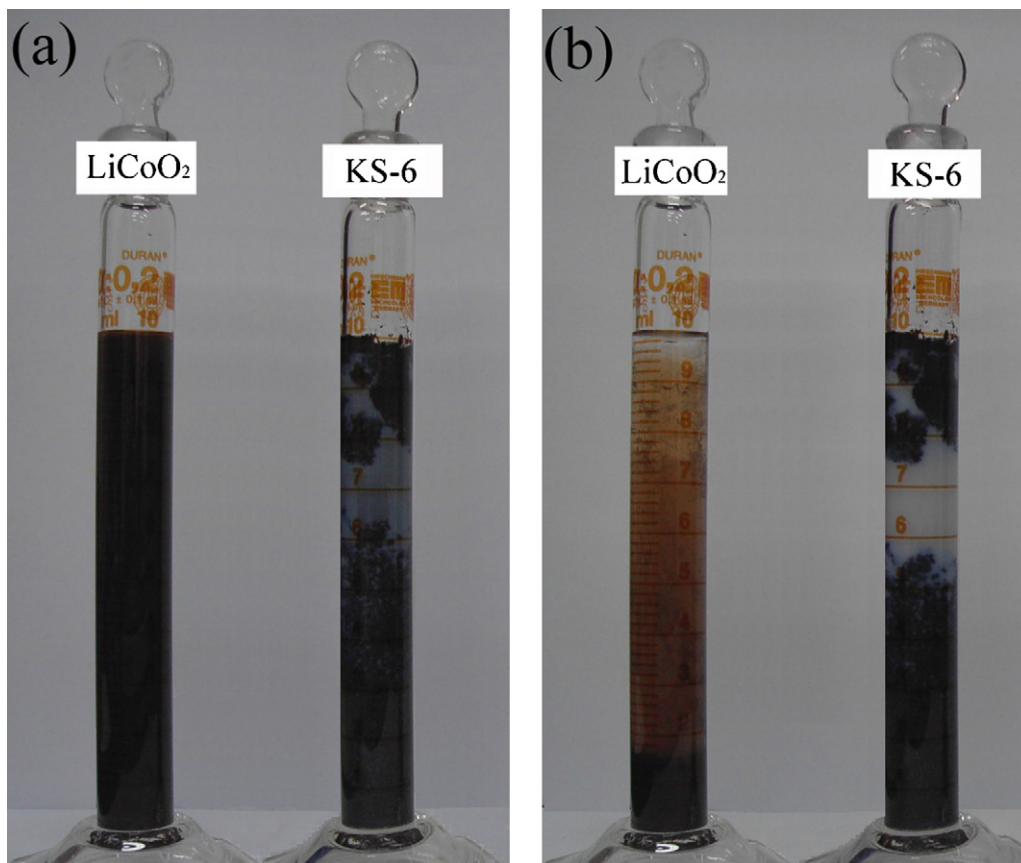


Fig. 4. The colloidal stability of 20 wt.% aqueous PBA-based binder suspensions with a respective addition of 10 wt.% powder of  $\text{LiCoO}_2$  and KS6 during different time periods of (a) 1 min and (b) 3 days.

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.

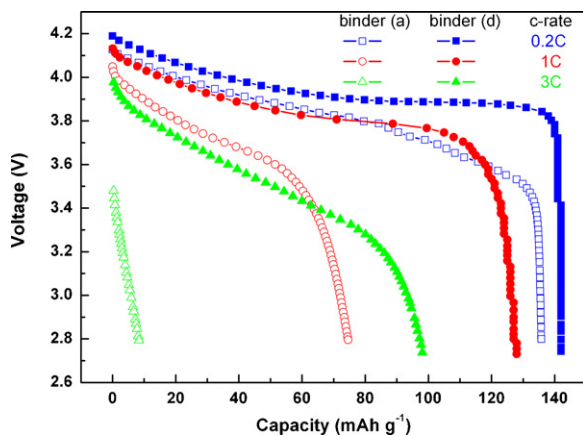


Fig. 5. Discharge curve at various discharge rates for  $\text{LiCoO}_2/\text{Li}$  half-cells prepared with respective additions of PA-based binder and PA-based binder + PBA-based binder.

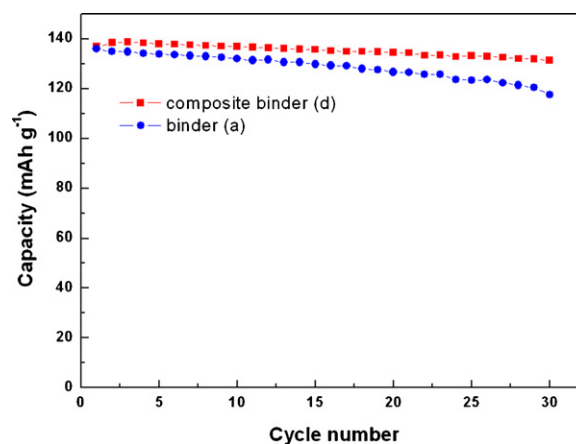


Fig. 6. Cycling stability of  $\text{LiCoO}_2/\text{Li}$  half-cells prepared with respective additions of PA-based binder and PA-based binder + PBA-based binder.

#### 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  $\text{LiCoO}_2$  cathode in lithium-ion batteries. From the

standpoint of  $\text{LiCoO}_2$ , 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  $\text{LiCoO}_2$  powder. Fortunately, the  $\text{LiCoO}_2$  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  $\text{LiCoO}_2$ . 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.

### Acknowledgment

The National Science Council of the Republic of China has provided funding for this study.

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