

Effects of pH on the dispersion and cell performance of LiCoO₂ cathodes based on the aqueous process

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Abstract The effects of the pH of a water-based slurry on the dispersion homogeneity and cell performance of lithium cobalt oxide (LiCoO₂) cathodes were investigated. Based on the results of dispersion and cell performance characterizations, it is known that the pH will affect the dispersion homogeneity of cathode materials and the resulting electronic conduction, adhesion strength and C-rate capability of as-prepared electrodes. For the LiCoO₂ aqueous slurry, the as-prepared electrode sheet is homogeneous at its initial equilibrium pH of 11.6 which is a safe distance away from its iso-electric point (IEP). However, this pH value is too high; the slurry would significantly react with the aluminum substrate to damage the microstructures of the sheets and the corresponding cell performances. Hence, the pH of an as-prepared LiCoO₂ slurry should be adjusted lower and kept away from the IEP as well.

Introduction

In the manufacturing process of lithium-ion cathodes, the compositions of cathode active material, conductive additive and polymer binders were initially mixed with solvent

to form a concentrated slurry and then cast on a conductive substrate, like aluminum (Al) foil [1–4]. To obtain a good electronic conduction between the as-cast sheet and the cathode current collector, adhesion between them is essential and needs to be considered. Because the adhesion depends on the dispersion properties of the slurry constituents, the cathode materials have to be homogeneously mixed in the initial stage to prepare a well-dispersed slurry [5–8]. According to the type of solvent used, the as-prepared slurry can be classified into two categories, a water-based (aqueous) system and an organic solvent-based (non-aqueous) system [9, 10], and the water-based system has attracted increasing attention due to environmental and cost considerations. Although the water-based system is a new process expected to have high potential, it is rarely used in the lithium-ion battery industry especially for the cathode, which may be due to the significant dissolution problems of LiCoO₂ in water [11] and the difficult to control dispersion properties of oxides [12].

It is commonly known that the pH value affects the surface chemistry of most oxides [12, 13], hence the influence of pH on the dispersion properties is expected and should be clarified for the study of the water-based battery process. In this paper, the importance of the effects of pH on the dispersion properties of aqueous slurries and the corresponding cell performances are shown. Because the LiCoO₂ is popular for the lithium-ion battery industry [14, 15], it was used as the cathode active material. The correlations between the pH and the surface chemistry of LiCoO₂, the dispersion behavior of aqueous slurries, and the electrochemical properties of as-prepared electrodes were studied. In addition, due to the fact that most metals are reactive with acids and bases, the effects of pH on the chemical stability of Al substrate was also studied.

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Experimental

The cathode active material used in this study was a high-purity LiCoO_2 powder (L106, LICO, Taiwan). The powder had a median size of $8.0 \mu\text{m}$ with a standard deviation of $0.45 \mu\text{m}$ measured by the light scattering (LS-230, Coulter Counter, USA) method. Synthetic graphite (Timrex KS6, Timcal A+G Sins, Switzerland) was used as a conductive agent. The binder used was a mixture of SBR (styrene butadiene rubber, Asahi Kasei Corporation, Japan) and SCMC (sodium carboxymethyl cellulose, Aldrich, USA) with a 3:2 weight ratio. The SBR was in the form of an aqueous emulsion of 48 wt% with a viscosity of 130 mPa·s at 25°C , and the SCMC was a thickening agent with an average molecular weight of 250,000 g/mol and substitution degree (DS) of 1.2. De-ionized water was used as a solvent in this study, and the pH was adjusted with solutions of hydrochloric acid and sodium hydroxide.

To investigate the dispersion properties of LiCoO_2 in aqueous suspensions, the technique of electroacoustic method (DT-1200, Dispersion Technology, USA) was used to measure its zeta-potential. Aqueous LiCoO_2 suspensions with different pH values were prepared by mixing 5 wt% powder in de-ionized water with and without the presence of SBR and SCMC, respectively. For the measurements of rheology, aqueous slurries were prepared and used by mixing 64.75 g (68.0 wt%) LiCoO_2 powder with additives of 4.20 g (6.1 wt%) graphite, 0.63 g (0.96 wt%) SBR and 0.42 g (0.64 wt%) SCMC. Note that the ratios of all additives were based upon LiCoO_2 powder. The slurries were de-agglomerated and mixed by ball milling with Y_2O_3 -stabilized ZrO_2 media for 24 h at room temperature. Rheological behavior of the slurries was determined using a concentric cylinder viscometer (AR1000, TA Instruments Ltd., UK).

The slurries prepared from the above compositions were cast on one side of Al foil by using a coma coater, and the average thickness of the LiCoO_2 sheets after drying and pressing were approximately 88 and 66 μm , respectively. The microstructures of cast LiCoO_2 electrode sheets were examined by a field emission scanning electron microscope (LEO-1530, LEO Electron Microscopy Ltd.). The surface resistance of each LiCoO_2 sheet was measured by a two-point resistance test using a MCP-TESTER FP analyzer, and the distance between the two-point probes was fixed at 1 cm. The adhesion strength for the LiCoO_2 sheet on the Al substrate was measured with a force gauge (DPX-1TR Model, IMADA Co., Ltd., Japan). Electrochemical performance was evaluated by assembling cathode-limited 2016 lithium coin cells. LiCoO_2 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_6 , 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, 1 and 3 C to 3.0 V.

Results and discussion

Surface chemistries of LiCoO_2

To investigate the effects of the pH value on the surface chemistry of active material, the zeta-potential of 5 wt% aqueous LiCoO_2 suspensions was measured as a function of pH with and without the presence of 0.96 wt% SBR and 0.64 wt% SCMC, respectively. As shown in Fig. 1, it was found that the LiCoO_2 has zero potential at $\text{pH} \sim 6$; this pH value is called its iso-electric point (IEP). At the IEP, the particles have a net surface charge of zero and will aggregate together. By increasing the shift of pH away from the IEP, the LiCoO_2 has higher surface potential and its dispersion stability is increased. When the SBR (curve (b)) or SCMC (curve (c)) is added, the IEP of LiCoO_2 shifts and the zeta-potentials become more negative and show near constant value in the pH range of 5–11. The shift of the IEP indicates that SBR and SCMC are specifically (or chemically) adsorbed on the LiCoO_2 . The SCMC compound has been known to dissociate more than 90% at $\text{pH} < 5\text{--}6$ [16] and the non-dissociated SBR should be pH-insensitive; thus adsorption of SBR or SCMC would shield the surface of LiCoO_2 to obtain a near constant zeta-potential at $\text{pH} 5\text{--}11$. It is also interesting to note that combined additions of both SBR and SCMC (curve (d)) showed that the zeta-potential result is closer to curve (b) but not the summation of curve (b) and (c). This implies that SBR

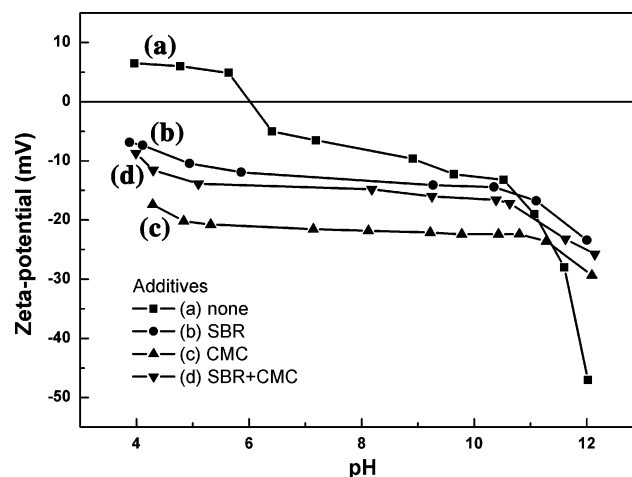


Fig. 1 Zeta-potentials of LiCoO_2 with and without presence of 0.96 wt% SBR and 0.64 wt% SCMC

has the priority of being adsorbed on LiCoO₂ and the adsorbed amount of SCMC will be minimized by competitive adsorption of SBR.

Dispersions of aqueous LiCoO₂ slurries

The effect of pH on the dispersion property of aqueous LiCoO₂ slurries was identified by analysis of rheology. The viscosities as a function of shear rate (γ) for aqueous LiCoO₂ slurries at pH values of 11.6, 9.3 and 5.7 were measured. Note that pH 11.6 is the equilibrium pH of an as-prepared slurry, and pH 9.3 and 5.7 are the pH-adjustment results. As shown in Fig. 2, shear-thinning behaviors, i.e. the decrease in viscosity with increasing shear rates, were observed for slurries with pH 11.6 and 9.3. This indicates some soft agglomerates existed in the slurries, and they were broken when an appropriate shear force was applied. As the pH value decreased to 5.7, a dilatant flow behavior, i.e. the viscosity increases with increasing shear rates, was obtained. The dilatant behavior suggests the presence of dramatically coagulated powders that can cause the 3-dimensional gel-type structure in slurries [17]. However, a reverse trend of decreasing viscosity with increasing shear rate was observed at $\gamma > 20 \text{ s}^{-1}$, and this should be due to the measuring errors of viscosity. A poorly dispersed slurry of pH 5.7 was found creeping out of the sample-clamping apparatus at $\gamma > 20 \text{ s}^{-1}$ and resulted in slowly decreasing the viscosity. According to the above rheologies, it is known that the slurry with pH 5.7 is least stable and has the worst dispersion properties, which agrees well with the results of zeta-potential measurements. As shown in Fig. 1, the IEP of LiCoO₂ is approximately 6, thus the LiCoO₂ will rapidly agglomerate at around pH 6 due to the lack of electrostatic repulsion between particles. It is also believed that the increasing negative potential due to the adsorption

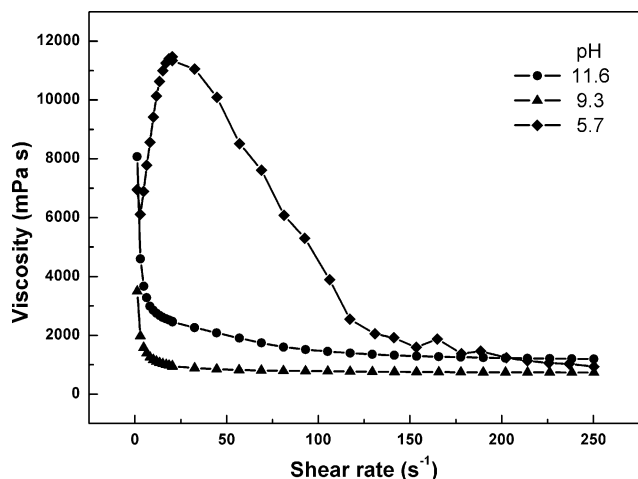
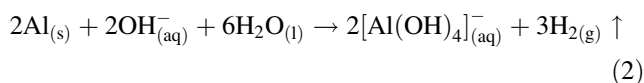
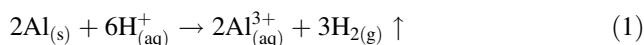


Fig. 2 Viscosity as a function of shear rate for 68.0 wt% aqueous LiCoO₂ slurries with equilibrium pH values of 11.6, 9.3 and 5.7

of SBR or SCMC would not be helpful for improving the dispersion properties because the agglomeration of LiCoO₂ was expected to occur before the chemically specific adsorption of binders.

Chemical stability of Al substrate

To investigate the effect of pH on the chemical stability of Al substrates, a piece of Al foil was immersed in de-ionized water having a pH value of 11.6, 9.3 and 5.7. For pH 11.6, a significant reaction and generation of gas at the interface between the Al foil and the water were observed, as shown in the photograph in Fig. 3. However, no significant reaction was observed at pH 9.3 and 5.7. This indicates that the Al substrate is chemically unstable at extremely basic conditions. In fact, Al has been known as an amphoteric metal that is reactive with acids (Eq. 1) and bases (Eq. 2) [18]. Generation of gas as shown in Fig. 3 is the evidence of the reaction in Eq. 2. In this experiment, the appropriate pH to avoid significant reactions as shown in the following is in the range of 1–11.



Due to the above results, it is known that Al substrates will be dissolved when the aqueous LiCoO₂ slurry, having



Fig. 3 Photographs showing the reaction of Al substrate in the aqueous solution of pH 11.6

an equilibrium pH of 11.6, is cast on its surface. Moreover, it is understood that this undesired phenomenon would be magnified under high temperature processes like casting and drying steps.

Microstructures of electrode sheets

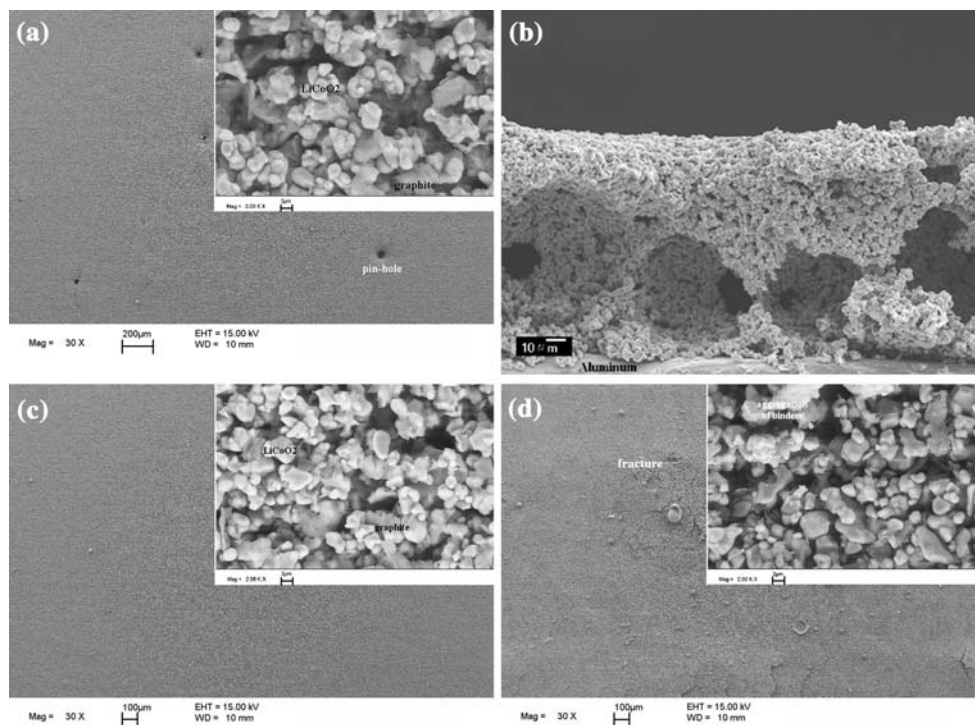
SEM characterized the effect of pH on the dispersion homogeneity of LiCoO_2 electrode sheets. The microstructures of sheets prepared from aqueous slurries of pH 11.6, 9.3 and 5.7 are shown in Fig. 4a–d, respectively. Components are labeled in the figures for easy identification. The insets of Fig. 4 are the corresponding images with high magnification. For the sheet of pH 11.6, the top-surface microstructure is homogeneous but with pin-holes (Fig. 4a), and its cross-sectional microstructure also shows many holes inside the sheet (Fig. 4b). The presence of these holes indicates that there was a great deal of gas generated and trapped during the casting and drying steps, which is the evidence of a chemical reaction between the basic slurry and the Al substrate (Eq. 2). When the pH is decreased to 9.3 (Fig. 4c), the microstructure still remains homogeneous but there are no holes inside the sheet. For the case of pH 5.7 (Fig. 4d), the sheet shows poor homogeneity with serious fractures and its microstructure shows significant aggregates of binders. The poor homogeneity of this sheet is caused by the agglomeration of LiCoO_2 at a pH near the IEP, and the aggregation of the binder is not only due to the agglomeration of its adsorbed powder but is

also caused by the unstable SBR when it makes contact with acid during the pH-adjusting process.

Adhesions, electronic conductions and cell performances of electrode sheets

To ascertain the effect of pH on the adhesion properties of electrode sheets, the adhesion strength between the as-cast LiCoO_2 sheet and the Al substrate as a function of pH was measured, as shown in Fig. 5. With decreasing pH, it was found that the adhesion strength increases from pH 13.5 to 9.3 and then, the adhesion strength, reversely decreases from pH 9.3 to 5.7. The best adhesion strength, at pH 9.3, occurred because of the good dispersion homogeneity of the constituents and the absence of sheet fractures which facilitate both the binding and the contact between powders and between the electrode sheet and the Al substrate. For pH 11.6, the weaker adhesion is due to the presence of fractures and thus the decreasing contact of the sheet on the Al substrate. For pH 5.7, the decreasing binding effect of the aggregated binders was the major reason for the weak adhesion in addition to the poor dispersion homogeneity. The figure also shows the surface resistance of the sheets as a function of pH. Interestingly, the resulting curve is just the opposite to that of adhesion strength. The resistance decreases from pH 13.5 to 9.3 and then increases from pH 9.3 to 5.7. This shows that the sheet with stronger adhesion has better electronic conduction, and it makes sense because

Fig. 4 SEM micrographs of LiCoO_2 electrode sheets prepared from pH of (a) 11.6 (top-view), (b) 11.6 (cross-section view), (c) 9.3 (top-view) and (d) 5.7 (top-view). The insets are the corresponding top-viewed microstructures with higher magnification



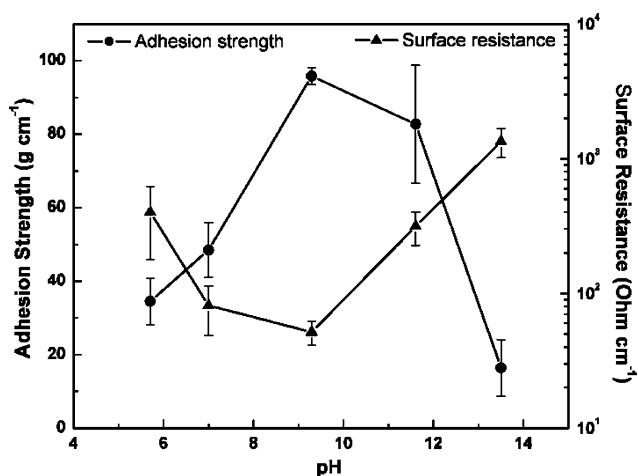


Fig. 5 The adhesion strength and the surface resistance of LiCoO₂ electrode sheets, as a function of pH

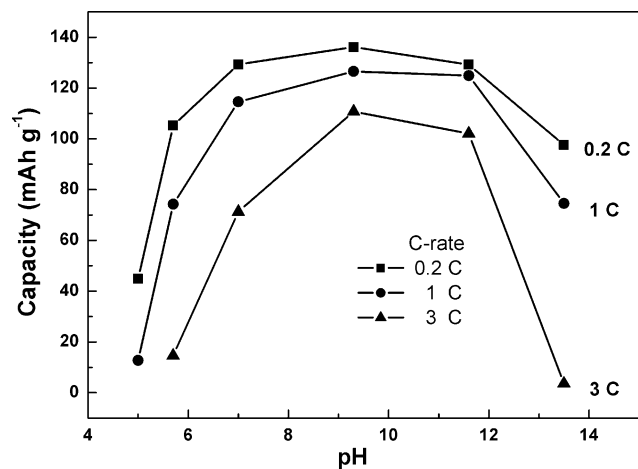


Fig. 6 Discharge curve at various discharge rates for LiCoO₂/Li half-cells as a function of pH

better adhesion would increase the electron transfer between the sheet and the Al substrate.

In order to further analyze the effect of pH on the electrochemical properties of the LiCoO₂ cathode, the C-rate performances at 0.2, 1 and 3 C were measured for each of the LiCoO₂ half-cells at different pH values, as shown in Fig. 6. At any of the discharged rates, it clearly shows that the cell with pH 9.3 has the highest capacity. This result agrees well with the measurements of surface resistance and adhesion strength, i.e. the lower surface resistance and higher adhesion yield better C-rate capability.

Conclusions

The effects of pH on the dispersion properties of aqueous LiCoO₂ slurries and the cell performance of as-prepared cathodes have been investigated. The dispersion analysis of

zeta-potential and rheology, show that the IEP of LiCoO₂ is around pH 6 and thus the slurry only has the appropriate dispersion properties at pH values that differ from 6. Near the IEP, the powders and binders aggregate and the slurry shows dilatant flow behavior that is undesired for a dispersion process. Although the electrode sheet has increasing dispersion homogeneity at pH values higher than 6, pH values that are too high will result in a chemical reaction between the slurry and the Al substrate and pH values that are too low will cause the binders to be unstable and form aggregates, which will damage the microstructures of the LiCoO₂ sheets. In the measurements of physical and electrochemical properties, it was found that the electrode sheets could have good properties of adhesion, electronic conduction and rate capability when they are homogeneously dispersed without the presence of fractures. Therefore, adjustment of the pH to reach the above requirements was essential and the appropriate value was found to be between the IEP and pH 11.6 for the aqueous LiCoO₂ slurries.

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