Direct micron-sized LiMn$_2$O$_4$ particle coating on LiCoO$_2$ cathode material using surfactant

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Abstract

Micron-sized LiMn$_2$O$_4$ particles were easily coated on LiCoO$_2$ cathodes using an amphoteric gelatin surfactant at pH $\approx 4–5$. The coated LiCoO$_2$ material showed a significantly higher thermal stability during charging and capacity retention on cycling at 4.6 V, compared to the bare LiCoO$_2$.

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1. Introduction

LiCoO$_2$ as a cathode material is mainly used in commercial Li-ion cells due to its high volumetric energy density and good cycling performance at elevated temperatures compared to LiMn$_2$O$_4$. However, the thermal stability of LiCoO$_2$ is inferior to that of LiMn$_2$O$_4$ at the charged states [1,2]. The reactivity of Li$_x$Mn$_2$O$_4$ with the electrolyte is less sensitive to variations in the $x$ values, but the reactivity Li$_x$CoO$_2$ increases rapidly as the value of $x$ is decreased [2]. Hence, delithiated Li$_x$CoO$_2$, depending on the $x$ value, can result in thermal runaway of the cell under thermal abuse conditions, sometimes catching fire or exploding [3–5]. In order to overcome this, Cho and Kim [6] reported that a sol–gel coating of LiMn$_2$O$_4$ on a LiCoO$_2$ cathode improved the stability of the cathode significantly. Even though this coating method improved the thermal stability of the cathode, the initial capacity after coating was reduced by 25 mA h/g, compared to the bare material, which required additional heat treatment at 800 °C in order for the surface coated LiMn$_2$O$_4$ to be fully crystallized. Otherwise, it impeded Li diffusion through the LiCoO$_2$ particle.

Surfactants consist of hydrophobic (water hating) and hydrophilic (water liking) groups, and the surfactant head group (S) and inorganic precursors (I) can be templated by electrostatic interactions, such as coulomb interactions, hydrogen bonding, and covalent bonding [7,8]. However, very few surfactants can be used in Li-ion cells, because they must be dissolved in a solvent. In addition, those containing Na$^+$ or K$^+$ ions should be excluded so they can be removed by filtering. If this does not occur, the electrochemical properties will be deteriorated by the Na$^+$ or K$^+$ ions.

In this paper, a direct micron-sized LiMn$_2$O$_4$ particle coating on a LiCoO$_2$ cathode using an ampho-
teric gelatin surfactant was reported to improve the thermal instability, and electrochemical properties of LiCoO₂.

2. Experimental

The micron-sized LiMn₂O₄ powder was prepared using the following procedure: a stiochiometric mixture of Mn acetate and Li acetate was dissolved in methanol with a small amount of citric acid as a chelating agent until a viscous gel solution was observed. This solution was dried and fired at 120 and 700 °C for 3 and 6 h, respectively. In order to effectively coat LiCoO₂ cathode particles, 100 g LiCoO₂ (average particle size 10 μm, BET surface area, 0.2 m²/g) and 25 g LiMn₂O₄ powders were used. The LiMn₂O₄ powders were ball-milled for 20 min in water (100 g) using 0.2 g of a polyacrylate dispersant, orotan® solution (chunghan Chem., Korea). The LiMn₂O₄ powder with orotan® was observed to be well dispersed in water without forming aggregates. To coat the dispersed LiMn₂O₄ powder on the cathode material, 0.8 g of gelatin was dissolved in 10 ml distilled water at 50 °C for 10 min, and then poured into 200 ml of distilled water. Gelatin was coated on the dispersed LiCoO₂ particles when the LiMn₂O₄ particles-dispersed orotan® solution was added. However, the pH of the gelatin needed to be adjusted to near its isoelectric point of pH ≈ 4–5 using acetic acid in order for the LiMn₂O₄ particles can be coated directly on the cathode particle [7]. At the isoelectric points, the –COOH end group in gelatin on the LiCoO₂ particles dissociates to –COO⁻, and a dehydration reaction occurs with the OH⁻ group created on the LiMn₂O₄ particle surface, which instantly results in a LiMn₂O₄ particle coating the cathode particles. The LiMn₂O₄ particle-coated LiCoO₂ particles then sank to the bottom of the beaker. This process normally took less than 30 s for the LiMn₂O₄-coated LiCoO₂ particles to sink completely to the bottom. The coated powder was then filtered and then vacuum-dried at 150 °C for 2 h.

The procedure for assembling a coin-type half-cell containing Li as an anode has been described in detail elsewhere [9]. The cathode consisted of 96 wt.% active material, 2 wt.% Super P carbon black, and 2 wt.% polyvinylidene fluoride. A mixture of ethylene carbonate/diethylene carbonate (EC/DEC) with 1.03 M LiPF₆ salts was used as the electrolyte.

Differential scanning calorimetry (DSC) experiments were carried out after charging the cell to 4.6 V at a 0.1 C rate. These were then disassembled in a glove box to obtained the charged cathode samples. All sample electrodes contained ~ 35 wt.% electrolytes, ~ 40 wt.% active material, ~ 23 wt.% Al foil, and ~ 2 wt.% carbon black/binder. Ten milligrams of the cathode composite were hermetically sealed in an aluminum DSC pan. The heating rate was 3 °C/min. Measurements on coin-type cells were cycled at between 2.75 and 4.3 V initially at 0.1, 0.5, and 1 C rates for each cycle. This was followed by continuous cycling at a 1 C (= 14 mA/g) rate for 27 cycles.

Fig. 1. (a) SEM micrograph of the micron-sized LiMn₂O₄ particle-coated LiCoO₂ particles. (b) EDX spectrum at the numbered spot.
3. Results and discussion

Fig. 1a shows the SEM micrograph of LiMn₂O₄ particle-coated LiCoO₂ powders. Submicron-sized LiMn₂O₄ particles appear to uniformly coat the LiCoO₂ particles. Since there was no separation of the LiMn₂O₄ particles from the LiCoO₂ surface after drying at 150 °C observed, a strong bond between the LiMn₂O₄ and LiCoO₂ particles was believed to have formed. Without using polyacrylate dispersant orotan® solution, as described above, the LiMn₂O₄ agglomerates could not be dispersed efficiently in water, resulting in a non-uniform coating on the LiCoO₂ particles. Dominko et al. [10] used gelatin only to coat the LiMn₂O₄ powder with carbon black but did not provide direct evidence for the carbon-black coating on the cathode particle. Energy-dispersive X-ray spectroscopy (EDX) of the particle (labeled as 1) indicated the presence of LiMn₂O₄ particles on the pristine LiCoO₂ sample, as shown in Fig. 1b. Fig. 2a shows the discharge curves of the bare LiCoO₂ and LiMn₂O₄ particle-coated LiCoO₂ samples. Even though the discharge capacity of the coated sample was smaller than that of the bare sample at the 0.2 C rate, showing 148 mA h/g, it was similar to the bare sample at a rate of 1 C, showing 142 mA h/g.

The capacity fading of the bare LiCoO₂ was faster than that of the coated material after 30 cycles at 1 C.

Fig. 2. Plots of (a) discharge curves of the bare and LiMn₂O₄-coated LiCoO₂ at 0.2, 0.5, and 1C rates and (b) discharge curves of the bare and LiMn₂O₄-coated LiCoO₂ after 1, 25, and 30 cycles at 1 C rate.
rate, holding only 23% of its initial capacity, while that of the cell containing the coated LiCoO₂ after 30 cycles was only 3%, as shown in Fig. 2b. This effect is believed to be the result of the micron-sized particle coating improving lithium diffusion into the active material. It should be noted that the initial capacity of the coated sample using the surfactant was larger than that derived from the sol–gel with 130 mA h/g [6].

DSC curves of the bare and coated cathode materials in the presence of the electrolyte are shown in Fig. 3. Zhang et al. [2] reported that the electrolyte provided a trigger for a violent exothermic reaction between the electrolyte/cathode material interface, and the cathode containing the electrolyte increased the exothermic reaction significantly in contrast to that without the electrolyte. Accordingly, a surface coating by a compound with a high thermal stability against the electrolyte reduced the amount of heat generated by the reaction between the electrolyte and the cathode, as was reported by Cho and Kim [6]. The decomposition reaction with the electrolyte initiating oxygen evolution from the cathode began to occur at 207 °C, which was followed by the development of intense exothermic peaks between 210 and 350 °C. However, the LiMn₂O₄ particle-coated LiCoO₂ showed an increased onset exothermic temperature of 230 °C with negligible heat generation from the exothermic reaction with the electrolyte. This indicates that the micron-sized LiMn₂O₄ particles coating is not only effective in retarding the decomposition of the charged LiₓCoO₂ but also in decreasing the exothermic heat.

4. Conclusions

A direct LiMn₂O₄ particle coating on a LiCoO₂ cathode material using surfactant gelatin significantly improved not only the capacity retention on cycling but also the thermal stability of the cathode material. Moreover, this coating method did not require a high temperature firing process, which is normally essential for the sol–gel coating method.

Acknowledgements

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References