



Direct micron-sized LiMn_2O_4 particle coating on LiCoO_2 cathode material using surfactant

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Abstract

Micron-sized LiMn_2O_4 particles were easily coated on LiCoO_2 cathodes using an amphoteric gelatin surfactant at $\text{pH} \cong 4-5$. 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_2O_4 . However, the thermal stability of LiCoO_2 is inferior to that of LiMn_2O_4 at the charged states [1,2]. The reactivity of $\text{Li}_x\text{Mn}_2\text{O}_4$ with the electrolyte is less sensitive to variations in the x values, but the reactivity Li_xCoO_2 increases rapidly as the value of x is decreased [2]. Hence, delithated Li_xCoO_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_2O_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_2O_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_2O_4 particle coating on a LiCoO_2 cathode using an ampho-

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teric gelatin surfactant was reported to improve the thermal instability, and electrochemical properties of LiCoO_2 .

2. Experimental

The micron-sized LiMn_2O_4 powder was prepared using the following procedure: a stoichiometric 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 LiCoO_2 cathode particles, 100 g LiCoO_2 (average particle size 10 μm , BET surface area, 0.2 m^2/g) and 25 g LiMn_2O_4 powders were used. The LiMn_2O_4 powders were ball-milled for 20 min in water (100 g) using 0.2 g of a polyacrylate dispersant, orotan[®] solution (chungnan Chem., Korea). The LiMn_2O_4 powder with orotan[®] was observed to be well dispersed in water without forming aggregates. To coat the dispersed LiMn_2O_4 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 LiCoO_2 particles when the LiMn_2O_4 particles-dispersed orotan[®] solution was added. However, the pH of the gelatin needed to be adjusted to near its isoelectric point of $\text{pH} \cong 4\text{--}5$ using acetic acid in order for the LiMn_2O_4 particles can be coated directly on the cathode particle [7]. At the isoelectric points, the $-\text{COOH}$ end group in gelatin on the LiCoO_2 particles dissociates to $-\text{COO}^-$, and a dehydration reaction occurs with the OH^- group created on the LiMn_2O_4 particle surface, which instantly results in a LiMn_2O_4 particle coating the cathode particles. The LiMn_2O_4 particle-coated LiCoO_2 particles then sank to the bottom of the beaker. This process normally took less than 30 s for the LiMn_2O_4 -coated LiCoO_2 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 carbo-

nate/diethylene carbonate (EC/DEC) with 1.03 M LiPF_6 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 obtain 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.

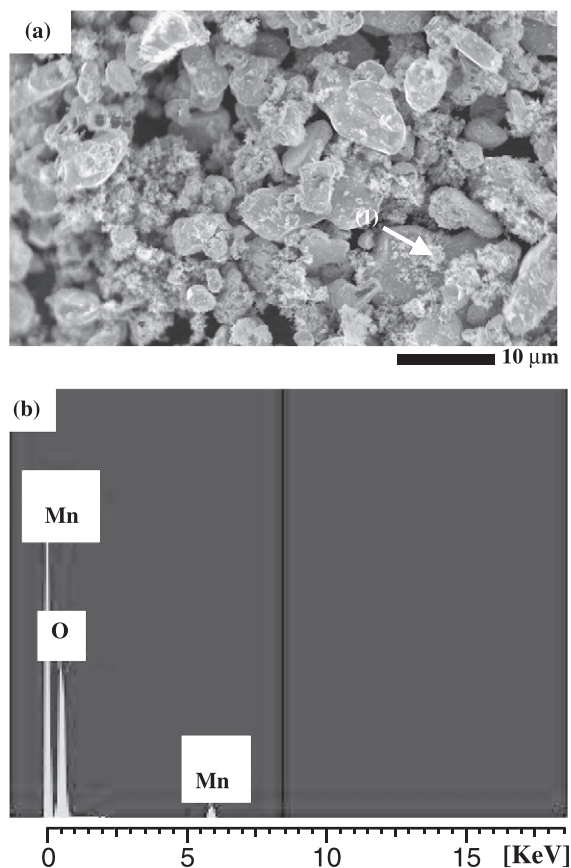


Fig. 1. (a) SEM micrograph of the micron-sized LiMn_2O_4 particle-coated LiCoO_2 particles. (b) EDX spectrum at the numbered spot.

3. Results and discussion

Fig. 1a shows the SEM micrograph of LiMn_2O_4 particle-coated LiCoO_2 powders. Submicron-sized LiMn_2O_4 particles appear to uniformly coat the LiCoO_2 particles. Since there was no separation of the LiMn_2O_4 particles from the LiCoO_2 surface after drying at 150°C observed, a strong bond between the LiMn_2O_4 and LiCoO_2 particles was believed to have formed. Without using polyacrylate dispersant or *Ortan*[®] solution, as described above, the LiMn_2O_4 agglomerates could not be dispersed efficiently in water, resulting in a non-uniform coating on the LiCoO_2 particles. Dominko et al. [10] used gelatin

only to coat the LiMn_2O_4 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 LiMn_2O_4 particles on the pristine LiCoO_2 sample, as shown in Fig. 1b. Fig. 2a shows the discharge curves of the bare LiCoO_2 and LiMn_2O_4 particle-coated LiCoO_2 samples. Even though the discharge capacity of the coated sample was smaller than that of the bare sample at the 0.2C rate, showing 148 mA h/g , it was similar to the bare sample at a rate of 1C , showing 142 mA h/g .

The capacity fading of the bare LiCoO_2 was faster than that of the coated material after 30 cycles at 1C

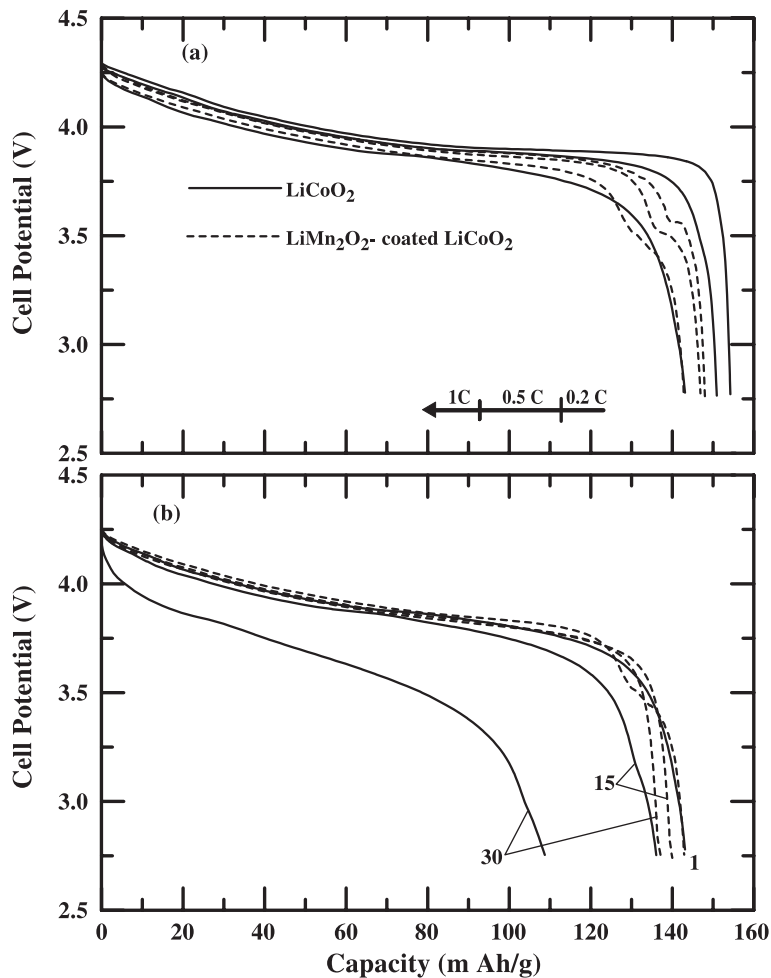


Fig. 2. Plots of (a) discharge curves of the bare and LiMn_2O_4 -coated LiCoO_2 at 0.2 , 0.5 , and 1C rates and (b) discharge curves of the bare and LiMn_2O_4 -coated LiCoO_2 after 1, 25, and 30 cycles at 1C rate.

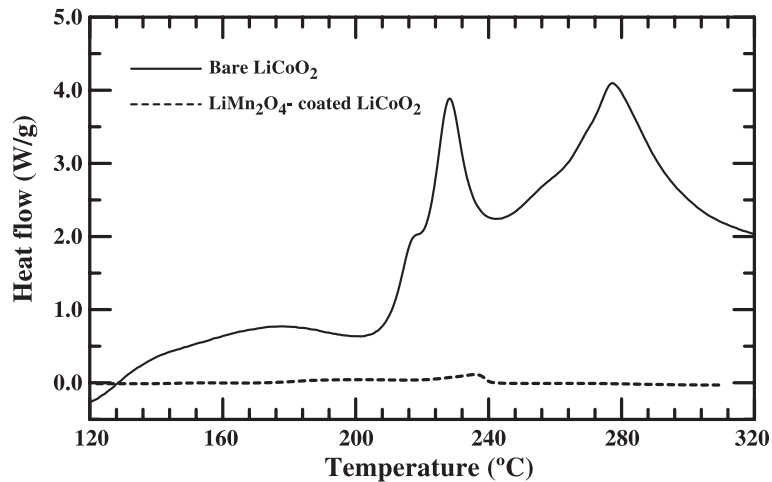


Fig. 3. DSC scans of the charged cathodes containing the bare and LiMn_2O_4 particle-coated LiCoO_2 materials. All the samples were equilibrated at 4.6 V prior to the DSC experiments. Each data set was measured at a heating rate of $3^\circ\text{C}/\text{min}$.

rate, holding only 23% of its initial capacity, while that of the cell containing the coated LiCoO_2 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 LiMn_2O_4 particle-coated LiCoO_2 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 LiMn_2O_4 particles coating is not only effective in

retarding the decomposition of the charged Li_xCoO_2 but also in decreasing the exothermic heat.

4. Conclusions

A direct LiMn_2O_4 particle coating on a LiCoO_2 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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