

Effect of conducting additives on the properties of composite cathodes for lithium-ion batteries

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Abstract In an attempt to achieve lithium-ion batteries with high rate capability, the effect of conducting additives with various shapes and contents on the physical and electrochemical performances was evaluated. Although the density of the cathode decreased upon the addition of the additives, the electrical conductivity and electrochemical performance were greatly improved. The composite cathodes with well-dispersed multi-walled carbon nanotubes (MWCNTs) exhibited excellent high rate capabilities and cyclabilities. In the case of cathode with 8 wt.% of MWCNTs (low density—LD), the highest discharge capacity of 136 mAh/g was obtained at 5 C-rate and capacity retention of 97% for 50 cycles was observed at 1 C-rate of discharge. The cathode with a mixture of 2 wt.% of Super P and 4 wt.% of MWCNTs (LD) also exhibits improved cycle

performances. The volume changes in the charge and discharge processes were successfully controlled by the bundles distributed between the host particles.

Introduction

As the intercalation hosts for the cathode of lithium-ion batteries, LiMO_2 ($M = \text{Co, Ni, Mn, Al, Mg, etc.}$) materials with a layered structure have been widely investigated. The performance of these materials depends on the relative composition of the compounds. Among these compounds, LiCoO_2 was proposed as the first viable cathode material, which exhibits a high energy density and excellent cycle life [1, 2].

In order to achieve high energy density lithium-ion batteries, it is important to achieve high material densities both intrinsically and extrinsically. The intrinsic density depends on the molecular weight and unit cell volume, and LiCoO_2 has the highest crystal density among these layered structures with various compositions. On the other hand, the extrinsic density can be controlled by adjusting the size and morphology of the particles. The single particle morphology of solid-state synthesized LiCoO_2 has a higher extrinsic density than the morphology with primary and secondary particles of mixed metals dioxide prepared by co-precipitation. For high power applications, the electronic and ionic conductivities of electrode materials are important. Another method of improving its conductivity is to mix the electrode material with conducting additives such as nano-sized carbon black.

Since the discovery of carbon nanotubes (CNTs), many investigations have been conducted in an attempt to achieve the homogeneous dispersion of CNTs in other materials [3–7]. The applications of CNTs as additives in lithium-ion

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Table 1 Densities and initial efficiencies of various cathodes

Additives	Electrode density (g/cm ³)	Initial efficiency (%)
Super P 2 wt.%	3.27	96.9
Super P 3 wt.%	3.21	97.2
Super P 5 wt.%	3.17	97.6
Super P 8 wt.%	2.85	97.3
Super P 2 wt.% + MWCNTs (LD) 1 wt.%	3.24	96.6
Super P 2 wt.% + MWCNTs (LD) 3 wt.%	2.91	97.0
Super P 2 wt.% + MWCNTs (LD) 4 wt.%	2.79	95.5
MWCNTs (HD) 3 wt.%	3.02	96.9
MWCNTs (HD) 5 wt.%	2.81	96.7
MWCNTs (HD) 8 wt.%	2.44	97.0
MWCNTs (LD) 3 wt.%	3.17	96.4
MWCNTs (LD) 5 wt.%	2.77	96.3
MWCNTs (LD) 8 wt.%	2.03	96.2

batteries have been reported as they exhibit improved high rate performances [8–12].

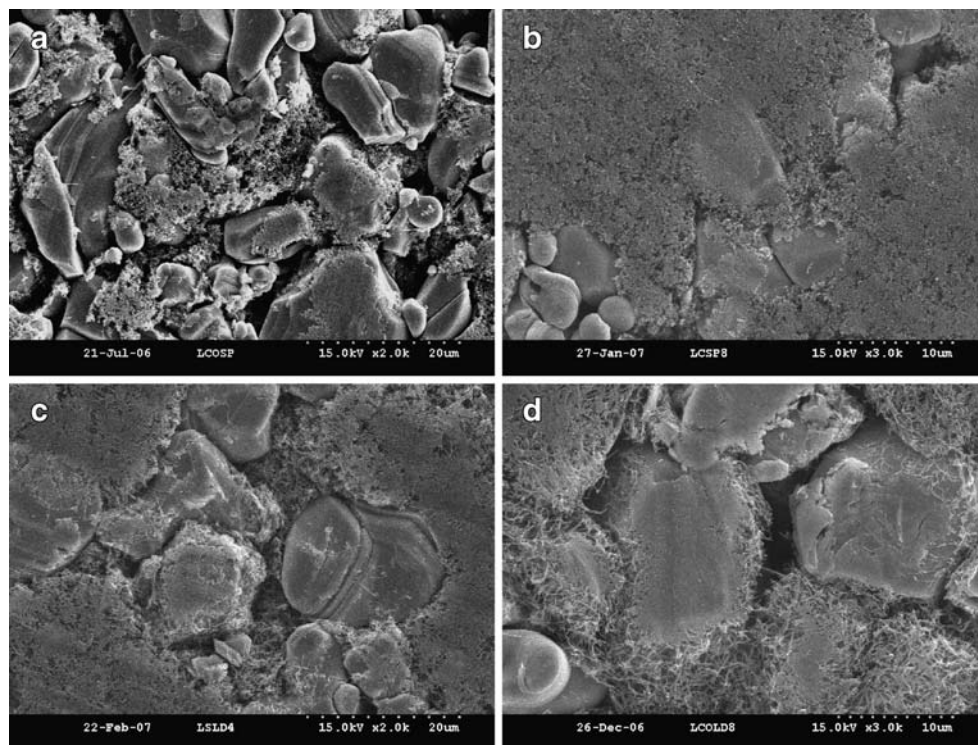
When lithium ions are extracted from a LiCoO₂ layered structure, the *c*-axis parameter starts to increase due to the repulsion between the CoO₂ slabs, and this results in the expansion of the unit cell volume [13]. The density and volume expansion of the electrode are important factors in the design of the cell. Repeated volume changes might bring about the deterioration of the electrodes due to the isolation of the host particles [14]. For high power applications, electrodes are designed to have low density and thickness, which can facilitate diffusion. However, a

low density is detrimental to electrical conductivity. In this regard, multi-functional additives have garnered much attention [12]. In this paper, the effects of multi-walled carbon nanotubes (MWCNTs) as an additive on the high rate capability and shelf life of lithium-ion batteries are reported.

Experimental

MWCNTs were synthesized by the vapor growth method of Nanokarbon in Korea [15]. The length and diameter of the

Fig. 1 SEM pictures of various cathodes of LiCoO₂ with **a** Super P 2 wt.%, **b** Super P 8 wt.%, **c** Super P 2 wt.% + MWCNTs (LD) 4 wt.%, **d** MWCNTs (LD) 8 wt.%



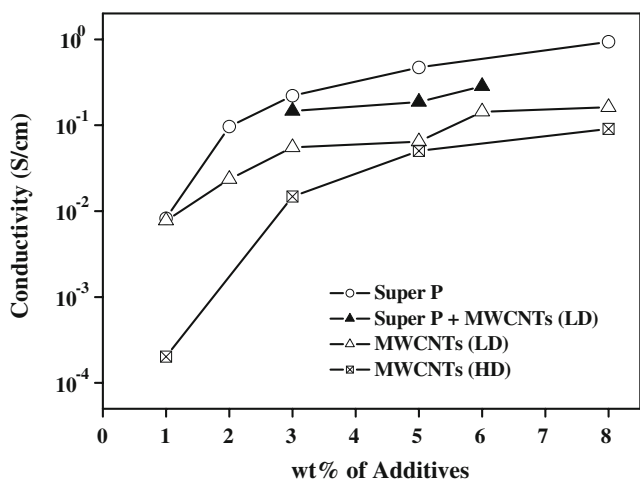


Fig. 2 Electrical conductivities of the composite electrodes with various contents of additives

MWCNTs were 10–20 μm and 60–80 nm, respectively. Low density (LD) and high density (HD) MWCNTs were used in this study. The particle size of the LiCoO_2 sample provided by LG Chem (Korea) was 10–20 μm . MWCNTs with a bundle-type shape are not easy to disperse in a viscous slurry. The MWCNTs and Super P carbon were dispersed in *N*-methyl-2-pyrrolidone in advance by ultrasonic treatment for 5 min. Appropriate amounts of these materials were mixed with a binder solution in a homogenizer at 5,000 rpm for 10 min. The weight ratio of solids to the polyvinylidene fluoride binder was 90:10. The composite slurries were coated on aluminum current collectors with a thickness of 30 μm , followed by drying in an oven for 30 min at 120°C. The typical values of the electrode

thickness after roll pressing were in the range of 70–90 μm . In order to evaluate the electrical conductivities of the composite electrodes by the van der Pauw method [16], samples were prepared by coating the slurry on a polyester film, which was then pressed and cut into square pieces with dimensions of 2×2 cm.

Electrochemical performances were evaluated using 2016-type coin cells. A lithium metal foil was used as the counter electrode and polypropylene film with a thickness of 18 μm was used as the separator. As the electrolyte, 1 M LiPF_6 in a mixture of ethylene carbonate, ethyl methyl carbonate, and diethyl carbonate (DEC) was used. The cycle range was 4.3–3.0 V vs. Li/Li^+ and the 1 C-rate was 150 mAh/g. The charge tests were carried out with a constant current of 0.1 C-rate for the first charge and the next charges were fixed at 0.2 C-rate. For the discharge tests, various constant currents in the range of 0.1–5 C-rate were applied to the cell one after another to evaluate the rate capabilities. For the cyclability tests, constant currents of 0.2 C-rate and 1 C-rate were used for charge and discharge, respectively.

Result and discussion

Table 1 shows the electrode densities and initial efficiencies for the composite cathodes with various compositions of the additives. In the case of the LiCoO_2 cathode of the commercial cell, an electrode density of 3.7 g/cm^3 is used in order to achieve a high energy density. The density of the cathode can be controlled by adjusting the pressing conditions. It is observed that an increase in the content

Fig. 3 Charge and discharge profiles at various C-rates: **a** Super P 2 wt.%, **b** Super P 8 wt.%, **c** Super P 2 wt.% + MWCNTs (LD) 4 wt.%, and **d** MWCNTs (LD) 8 wt.%

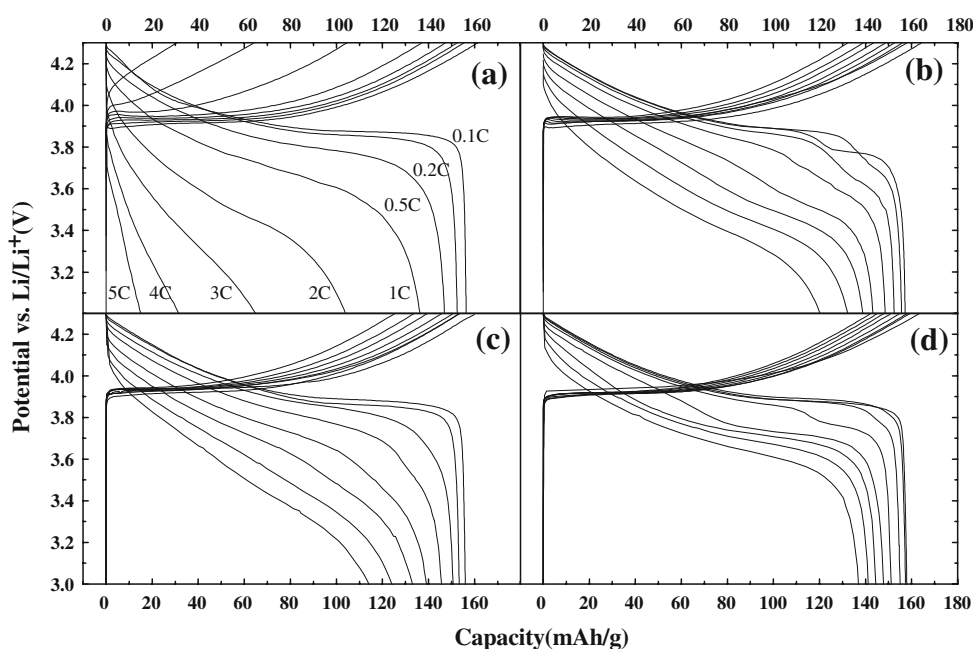
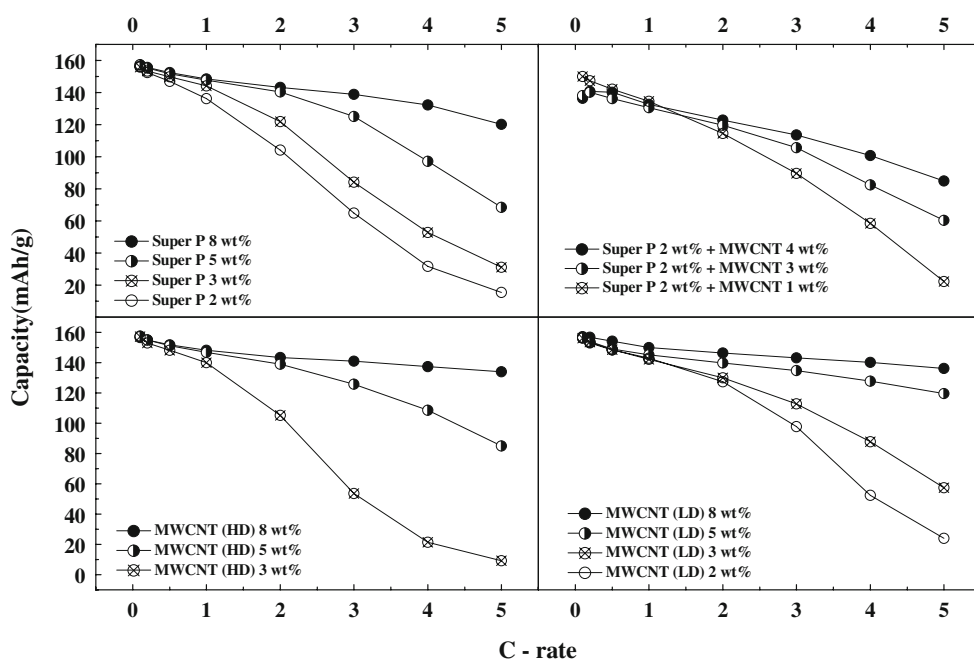


Fig. 4 Summary of gravimetric discharge capacities at different C-rates for various composite electrodes



of the additive lowers the electrode density and that the samples with MWCNTs (LD) tend to give the lowest values for a given content of additives. Figure 1 shows the scanning electron microscopy (SEM) pictures of the morphologies of the various composite cathodes. Increasing the amount of Super P carbon caused the agglomerated particles to spread over the LiCoO_2 . In the case of the MWCNTs, the bundles that formed were dispersed between the host particles. In the case where a completely divided form of Super P carbon is used, a single nano-sized particle can provide a point contact between two LiCoO_2 particles. On the other hand, a tube separated from the bundles can easily connect neighboring particles by a line contact. However, the perfect individual separation of the CNTs is hard to achieve. Our strategy is to break the bundles and to distribute the divided smaller bundles between the host particles.

As shown in Fig. 2 and Table 1, among the samples with the various additives, relatively high conductivities were observed in the samples with Super P. This result is attributed to the difference in the electrode densities after pressing. In the case of the MWCNTs, the HD samples have higher electrode densities than the LD samples. On the other hand, the LD samples exhibit higher conductivities than the HD samples. This might be due to the poor distribution of the MWCNTs (HD).

Figure 3 shows the charge and discharge profiles of the cathodes with various additives. In the case of cathode with 8 wt.% of MWCNTs (LD), the highest discharge capacity of 136 mAh/g was obtained at 5 C-rate and this is about 86% of discharge capacity at 0.1 C-rate. The gravimetric discharge capacities of the different composite cathodes at

various C-rates are summarized in Fig. 4. The cathodes with the MWCNTs (LD) exhibit excellent high rate capabilities. Increasing the amount of the additive improves the electrical conduction in the electrode. In addition, the bundle nature of the MWCNTs leads to the relatively low density and high flexibility of the electrode. These might facilitate the wetting of electrolyte and the diffusion of lithium ions at high C-rates. Figure 5 shows the cycle performances of the various composite cathodes. The cathodes with MWCNTs and a mixture of Super P and MWCNTs exhibit improved cycle performances. In the case of cathode with 8 wt.% of MWCNTs (LD), capacity retention of 97% for 50 cycles was obtained. The addition of the MWCNTs to the cathode delayed its deterioration, by

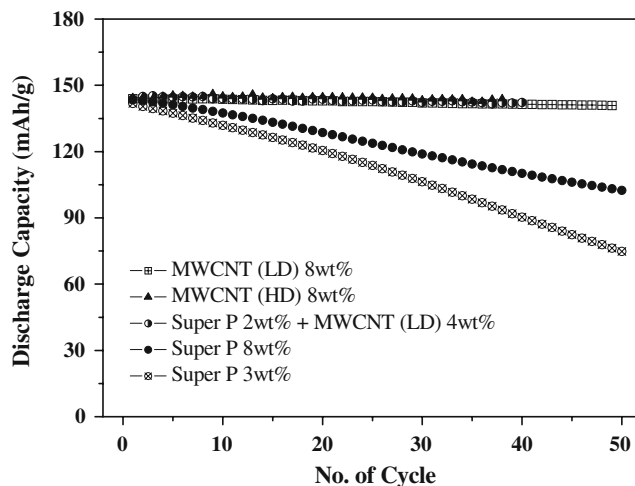


Fig. 5 Cycle performances of various composite cathodes

allowing the control of the volume change for repeated charge and discharge.

Conclusions

Vapor-grown MWCNTs were used as a new additive in lithium-ion batteries. The densities and electrical conductivities of the cathodes depended on the amount and morphology of the additives. A high rate capability and excellent cycle life were achieved when using a dispersion of MWCNTs in the cathode. The MWCNT bundles were able to maintain the contacts between the host particles and help to transport electrons during the repeated cycling. The applications of high power electrodes incorporating MWCNTs are highly anticipated.

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