Effect of LiCoO_2 Cathode Density and Thickness on Electrochemical Performance of Lithium-Ion Batteries

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ABSTRACT:

The consequences of electrode density and thickness for electrochemical performance of lithium-ion cells are investigated using 2032-type coin half cells. While the cathode composition is maintained by 90:5:5 (wt.%) with LiCoO_2 active material, Super-P electric conductor and polyvinylidene fluoride polymeric binder, its density and thickness are independently controlled to 20, 35, 50 μm and 1.5, 2.0, 2.5, 3.0, 3.5 g cm^{-3} , respectively, which are based on commercial lithium-ion battery cathode system. As the cathode thickness is increased in all densities, the rate capability and cycle life of lithium-ion cells become significantly worse. On the other hand, even though the cathode density shows similar behavior, its effect is not as high as the thickness in our experimental range. This trend is also investigated by cross-sectional morphology, porosity and electric conductivity of cathodes with different densities and thicknesses. This work suggests that the electrode density and thickness should be chosen properly and mentioned in detail in any kinds of research works.

Keywords: Electrode density; Electrode thickness; Electrode loading; Electrode porosity; Electrochemical performance; Lithium-ion batteries

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1. Introduction

Even though lithium-ion batteries (LIBs) have been the dominating energy storage devices due to their high energy densities and excellent cycle lives,¹⁻³⁾ there are still some technical issues such as much higher energy density, shorter charging time, longer cycle life, and lower cost per kWh for battery-electric vehicles (BEVs) and energy storage systems (ESSs). Especially, since the high energy density is closely related to the vehicle mileage and price, lots of researchers have focused on new electrode active materials with higher gravimetric and volumetric capacities.⁴⁻⁷⁾ However, the high energy density can be achieved by not only high-capacity electrode active

materials but also higher electrode density and thickness with conventional commercial materials. The latter has sometimes been considered as more important factors by many manufacturers. Unfortunately, there are limited research works on electrode design parameters such as density and thickness,⁸⁻¹⁵⁾ and moreover they are not various and wide enough to understand many parameters in a variety of points of view.

Shim *et al.*⁸⁻¹⁰⁾ firstly examined effects of anode density and thickness on irreversible capacity loss, electric conductivity change, and electrochemical properties with a few commercial natural graphites. As for cathode active materials, Zheng *et al.*¹¹⁻¹³⁾ controlled the cathode porosity from 50% to 0% while maintaining the electrode loading level, which meant that the thickness would be thinner with decreasing porosity, and found some relationship between porosity and electrochemical performance. Recently, Chen

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*et al.*¹⁴⁾ and Cho *et al.*¹⁵⁾ tried to correlate experimental electrochemical data with simulated results under different porosity and thickness conditions, respectively. However, even though each previous work can give useful information on specific electrode design parameter effects, all of them did not control both density and thickness simultaneously. Moreover, in order to penetrate large-format LIBs into BEV and ESS markets successfully, these two design factors should be investigated in a variety of test conditions.

In this work, we manufacture lots of LiCoO₂ cathodes with five different densities (1.5, 2.0, 2.5, 3.0, 3.5 g cm⁻³) and three different thicknesses (20, 35, 50 μm). And then, after the fifteen LiCoO₂ cathodes are assembled to 2032-type coin half cells, their rate capability from 0.1C to 20C and 1C cycle lives are evaluated at room temperature. In order to understand the density effect more clearly, the cross-sectional morphology, porosity and electric conductivity of cathodes with different densities under the same thickness are also measured or analyzed.

2. Experimental

2.1. Cathode preparation

Cathodes were prepared by coating an N-methyl-2-pyrrolidone (NMP, Sigma-Aldrich, USA) based slurry consisting of 90 wt.% LiCoO₂ (10 μm, KD-10, Umicore Korea, Korea), 5 wt.% conductive carbon (Super-P, Timcal, Switzerland), and 5 wt.% polyvinylidene fluoride (PVdF, KF-1300, Kureha, Japan) binder onto Al current collector foil (15 μm, Sam-A Aluminium, Korea). The cast cathodes with different densities and thicknesses were dried in air at 130°C for 1h, and then they were roll-pressed to get targeted densities (1.5, 2.0, 2.5, 3.0, 3.5 g cm⁻³) and thicknesses (20, 35, 50 μm) with a gap-control-type roll pressing machine (CLP-2025, CIS, Korea). Each cathode was punched to a disc of 12 mm diameter and subject to be dried at 80°C for 12 h under vacuum. The active material loading level of cathodes in this work ranges from 3.72 to 18.05 mg cm⁻², which is originated from measured density and thickness like Table 1.

2.2. Morphological and electrical analysis of cathodes

The surface and cross-sectional morphologies of cathodes with different densities and thicknesses were characterized by normal scanning electron microscope

Table 1. Physical properties of prepared LiCoO₂ with different densities and thicknesses

ID	Electrode Density (g cm ⁻³)	Electrode Thickness (μm)	Loading Level (mg cm ⁻²)	Calculated Porosity (%)
D1.5 T20	1.62	23	3.72	62.8
D1.5 T35	1.59	35	5.58	63.3
D1.5 T50	1.61	50	8.05	62.9
D2.0 T20	2.04	20	4.07	53.2
D2.0 T35	2.01	37	7.43	53.8
D2.0 T50	1.93	49	9.47	55.5
D2.5 T20	2.61	21	5.49	39.8
D2.5 T35	2.45	35	8.58	43.6
D2.5 T50	2.39	50	11.95	45.0
D3.0 T20	2.91	24	6.99	33.0
D3.0 T35	2.86	35	10.00	34.2
D3.0 T50	3.10	52	16.11	28.7
D3.5 T20	3.39	23	7.79	22.0
D3.5 T35	3.54	35	12.39	18.5
D3.5 T50	3.47	52	18.05	20.1

(SEM, JSM-6390, JEOL, Japan) and field emission scanning electron microscope (FE-SEM, S4800, Hitachi, Japan), respectively. In order to prepare a cross-sectional specimen of each cathode, it was cut by an argon-ion beam polisher (E3500, Hitachi) at a constant power of 2.1 W (6 kV and 0.35 mA) under vacuum (< 2.0 × 10⁻⁴ Pa).

The porosities of cathodes were calculated from apparent electrode volume, electrode mass, cathode composition, and the true density of each component (LiCoO₂, Super-P and PVdF) according to the following equations.

$$\text{Porosity(\%)} = \frac{V_{CA} - V_{CA}^{filled}}{V_{CA}} \times 100 \quad (1)$$

$$V_{CA}^{filled} = \frac{m_{CA}}{(\rho_{AM} \times x_{AM}) + (\rho_{CC} \times x_{CC}) + (\rho_{PB} \times x_{PB})} \quad (2)$$

where V_{CA} is the measured apparent electrode volume without Al current collector, V_{CA}^{filled} is the calculated electrode volume filled with electrode components, m_{CA} is the mass of all the electrode components, x_{AM} , x_{CC} and x_{PB} are the percentages of active material (LiCoO₂), conductive carbon (Super-P) and polymeric binder (PVdF) within the electrode while

ρ_{AM} , ρ_{CC} and ρ_{PB} are the true density for active material, conductive carbon and polymeric binder, respectively. The true densities for LiCoO_2 , Super-P and PVdF are 5.1, 1.95 and 1.78 g cm^{-3} , respectively.

The electric conductivities of the cathodes were determined with a four-point probe measurement system (CMT-SR1000N, Chang Min Tech, Korea), in which the four-point probe was provided by Jandel Eng. As an effort to obtain and compare real electric conductivity values, all the measurements were carried out with the prepared cathodes on Al current collector, which were placed upon non-conductive and hard Si wafer to prevent sharp probes from penetrating cathodes.

2.3. Cell assembly and electrochemical testing

To evaluate the rate capability and cycle performance of the cathodes with different densities and thicknesses, fifteen kinds of LiCoO_2 cathodes were assembled to 2032-type coin half cells with Li metal (450 μm , Honjo Metal, Japan) as an anode, polyethylene (PE) separators (thickness: 20 μm , 520H, SK Innovation, Korea) and 1M LiPF_6 in ethylene carbonate (EC)/diethylene carbonate (DEC) (1/2, by volume, PANAX ETEC, Korea) as an electrolyte. After assembly, the unit cells were aged for 12 h, and then cycled between 3.0 and 4.2 V at a constant current (CC) of C/10 rate in both charging and discharging processes as a formation step using a charge/discharge cycler (PNE Solution, Korea) at 25°C . In order to stabilize the unit cells, they were cycled between 3.0 and 4.2 V at a little higher current density of 0.2C for additional 3 cycles. We call these two steps as a precycling. The rate capability of each unit cell was evaluated by increasing discharging current densities from 0.1 to 20C (0.1, 0.2, 0.5, 1, 2, 5, 10, and 20C) in a CC mode while maintaining the charging current density of 0.2C in a constant current/constant voltage (CC/CV) mode. After this rate capability test, the corresponding unit cells were subject to be cycled at a high current density (1C rate, CC in discharge and CC/CV in charge between 3.0 and 4.2 V) for 50 cycles.

3. Results and Discussion

In this work, the most important point is to prepare fifteen different kinds of LiCoO_2 cathodes to get targeted densities and thicknesses. However, due to the experimental limitation in practice, it was not easy to

control the density and thickness exquisitely at the same time. Anyhow, along with target values, the measured density, thickness, loading level, and calculated porosity of the corresponding cathode are summarized in Table 1. Each cathode is denoted as “Dxx Tyy”, where D and T indicate its density and thickness while xx and yy mean their target values, not measured, respectively. For example, the D1.5 T20 indicates the LiCoO_2 cathode with 1.5 g cm^{-3} and 20 μm . Although there are small deviations around $\pm 0.1 \text{ g cm}^{-3}$ and $\pm 3 \mu\text{m}$ in the density and thickness, respectively, these values are too tiny to give big effects on physical and electrochemical properties of cathodes.

When the thickness increases under the same density, the corresponding loading level also increases proportional to its thickness while the pore structure is well maintained. In the other hand, the cathode porosity is strongly dependent on its density, and about 10% porosity decrease is found as the density is increased by 0.5 g cm^{-3} . When the cathode density reaches to 3.5 g cm^{-3} , its porosity level becomes down to around 20%, which is thought to be the commercially highest cathode density level, 4.0 g cm^{-3} , for mobile IT application, in which the top priority is the energy density.

First of all, the porosity change of cathodes is investigated by the surface and cross-sectional morpholo-

Fig. 1. Surface SEM images of 50 μm LiCoO_2 cathodes with different densities (a) D1.5 T50, (b) D2.0 T50, (c) D2.5 T50, (d) D3.0 T50, and (e) D3.5 T50.

gies. Since there were no big differences depending on thickness changes, the SEM images of the only 50 μm cathodes with different densities (D1.5 T50, D2.0 T50, D2.5 T50, D3.0 T50, and D3.5 T50) are presented in Fig. 1 and 2. As a point of surface pore structure, at the density of 3.0 g cm^{-3} , the surface morphologies are greatly changed from loosely to densely packed structure. Lots of big pores and loosely distributed inactive components are observed in the Fig. 1(a), (b) and (c), whereas, as shown in Fig. 1(d) and (e), the active materials are well rearranged and deformed to give very flat and packed surface morphology without big pores. It means that less amount of electrolyte can soak into high density cathodes, thereby resulting in poor rate capability.

In order to investigate the inner pore structure of cathodes, which are also used for Fig. 1, cross-sectional morphologies of corresponding cathodes are presented in Fig. 2. Similar to the surface morphologi-

cal changes, the inner pores seem to be disappeared through the active material rearrangement and inactive components compression as a function of density. In addition, the surface top layer of the cathodes is readily changed from rough to flat line.

This kind of porosity reduction will inevitably cause higher electrode resistance due to insufficient liquid electrolyte amount around cathode active materials. However, the electric conductivity can be enhanced by better contact property between active materials and electric conductors.¹⁶⁾ So, the electric conductivities of the only 50 μm cathodes are measured and summarized in Table 2. As the cathode density increases, its electric conductivity is continuously improved as we expected. Especially, there seems to be slow progress in electric conductivity up to the 2.5 g cm^{-3} density, however, electric conductivity jumping is found over the 3.0 g cm^{-3} density, which is well matched with pore structural changes in Fig. 1 and 2. However, we should mention again that our electric conductivity is measured with the real cathode coated on Al current collector, if too high electric conductivity values sound controversial comparing to the previous work,¹²⁾ in which cathode layer was coated on non-conductive glass substrate. Moreover, this four-point probe measurement can give reliable results only if the cathode thickness is around or higher than 50 μm . When the thickness is less than 50 μm , we cannot get a reproducible data.

From these experimental data, the electric conductivities of cathodes are highly improved by increasing their densities, however the decreased porosity of cathodes may cause some negative effects on lithium ion conductivity within the cathode pores. In order to investigate these trade-off properties in the real system, fifteen different kinds of cathodes are assembled to 2032-type coin half cells and evaluated according to rate capability and cycle testing methods.

Regardless of densities and thicknesses, all the coin cells show similar specific capacity of 140 mAh g^{-1} with a coulombic efficiency in the range of 96~97% during the first formation step. Moreover, as shown in

Fig. 2. Cross-sectional SEM images of 50 μm LiCoO_2 cathodes with different densities (a) D1.5 T50, (b) D2.0 T50, (c) D2.5 T50, (d) D3.0 T50, and (e) D3.5 T50.

Table 2. Electric conductivities of 50 μm LiCoO_2 cathodes with different densities

	D1.5 T50	D2.0 T50	D2.5 T50	D3.0 T50	D3.5 T50
Electric Resistivity ($\text{m}\Omega \text{ cm}$)	37.353	18.635	15.901	3.725	0.131
Electric Conductivity (S cm^{-1})	25.9	53.7	62.9	268.5	7610.4

*Electrode with Al current collector

Fig. 3. Charge/discharge voltage profiles of LiCoO₂/Li coin cells containing 20 μm cathodes with different densities from 1.5 to 3.5 g cm^{-3} .

Fig. 3, their voltage profiles are very similar each other, which means that all the cathodes in this work

are well prepared. After the precycling including one formation step and additional three stabilization cycles, they are subject to be cycled for rate capability and cycle life. Firstly, the rate capabilities of cathodes as a function of density under the same thicknesses are shown in Fig. 4. As mentioned in the experimental part, only discharge current densities are changed from 0.1 to 20C while maintaining the charge current density as 0.2C. Clearly, the capacity retention behavior is largely improved especially over 5C current density when the density is low under the same thickness condition. In other words, higher electrode porosity is the more important factor for rate capability than better electric conductivity. Moreover, we can observe big capacity drops at 20C and 5C for the 20 μm and 50 μm cathodes from the density value of 3.0 g cm^{-3} , as suggested from the morphological study in Fig. 1 and 2.

Fig. 4. Rate capability of LiCoO₂ cathodes with different densities under the same thickness of (a) 20 μm , (b) 35 μm and (c) 50 μm .

Fig. 5. Rate capability of LiCoO₂ cathodes with different thicknesses under the same density of (a) 1.5 g cm^{-3} , (b) 2.0 g cm^{-3} , (c) 2.5 g cm^{-3} , (d) 3.0 g cm^{-3} , and (e) 3.5 g cm^{-3} .

Fig. 6. Cycle performances of LiCoO₂ cathodes with different densities under the same thickness of (a) 20 μm , (b) 35 μm and (c) 50 μm .

Fig. 7. Cycle performances of LiCoO₂ cathodes with different thicknesses under the same density of (a) 1.5 g cm^{-3} , (b) 2.0 g cm^{-3} , (c) 2.5 g cm^{-3} , (d) 3.0 g cm^{-3} , and (e) 3.5 g cm^{-3} .

Meanwhile, because there is little difference even at 20C current rate among 20 μm cathodes with low densities (D1.5 T20, D2.0 T20 and D2.5 T20), which mean high porosities, the electrode thickness should be considered with the density altogether.

In order to evaluate the thickness effect on rate capability more clearly, all the rate capability data are redrawn to be expressed a function of thickness under the same density like Fig. 5. The effects of cathode thickness on rate capability are found to be more influential than the density, in which the 5C seems to be a critical current rate except for the 3.5 g cm^{-3} cathodes being distinguished from 2C. However, even in the lowest density level, 1.5 g cm^{-3} , the 50 μm cathode cannot deliver proper capacity at high current rates such as 10 and 20C. After the c-rate capability test, each cell is subjected to be cycled at 1C rate for 50 cycles. Since the cells are also charged at 1C rate in a CC/CV mode, we can easily evaluate the density and

thickness effect on their cycle performances. Each cycle performance depending on density and thickness is presented in the Fig. 6 and 7, respectively. When the thickness is sufficiently low around 20 μm , no capacity fading is found regardless of densities. However, when the thickness is equal to or higher than 35 μm , it is clearly observed that the capacity retention behavior becomes better when the cathode density is low. Among the 50 μm cathode series, all of them could not maintain their initial capacity values at the 50th cycle.

The thickness effect on cycle performance can be clearly confirmed by the Fig. 7. As the cathode density is increased, the cycle performances of unit cells with the thicknesses equal to or higher than 35 μm dramatically becomes worse. However, the D1.5 T50 cathode shows even worse cycle life comparing to D2.0 T50 and D2.5 T50 cathodes. This unexpected result can be ascribed to the fact that the roll-pressing process was not applied to the D1.5 T50 cathode due to its suffi-

ciently high electrode density just after casting and solvent drying. So, the roll-pressing step for high thickness cathodes should be taken to guarantee certain cycle performances.

From the above results, we can deliver well-designed and detail experimental results for the density and thickness effects of LiCoO₂ cathodes on representative electrochemical performances. Although this work cannot cover all of various cathode or electrode systems, it will be a good guidance for many LIB researchers.

4. Conclusion

The effects of electrode density and thickness on rate capability and cyclability are systematically investigated with fifteen different LiCoO₂ cathodes. As the density is increasing from 1.5 to 3.5 g cm⁻³, both rate capability and cyclability become worse due to largely decreased porosity, which is confirmed by the surface and cross-sectional SEM images, regardless of electric conductivity enhancement. However, the thickness effect is found to be the more dominating factor towards electrochemical performances. In addition, we think that this work can be a good guideline for battery researchers to evaluate and compare their electrochemical data.

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