

Improvement of Lithium-Ion Battery Performance by Two-Layered Slot-Die Coating Operation

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The cathode and anode electrodes in lithium-ion batteries typically contain a significant proportion of particles and binders. During the electrode drying process, high temperature will lead to the binder migration phenomenon. Uneven particle/binder distribution can cause poor adhesion between coating and substrate, disruption of conductive paths, and decrease in electrode performance. In this study, a two-layered cathode was designed by using separate compositions of

slurry ingredients in each layer, as produced by means of a simultaneous multilayer coating method. The two-layered cathode with the top layer containing less binder than the bottom layer yielded a better particle/binder distribution in the final structure under high-temperature drying. A battery made with the two-layered cathode appeared to give a better overall performance.

Introduction

Lithium-ion batteries (LIBs) have been widely applied to computer, communication, and consumer electronics (3C) products and in vehicles, such as electric vehicles (EVs), hybrid electric vehicles (HEVs), and plug-in hybrid electric vehicles (PHEVs) in recent years. As consumer demand has increased over the years, it has become necessary for LIB manufacturers to look for ways to improve the production rate and product quality, without increasing the cost.^[1–3] In the manufacture of LIB electrodes, the drying process is one of the major factors that determines the production rate and cost. The conventional method for drying the electrodes in LIBs is to use forced convection air drying. The drying temperature and air flow rate are the main parameters that control the dried electrode quality.^[4,5] Because the energy density requirement for LIBs used in EVs is much higher than that of 3C batteries, a thicker electrode containing more active material has to be used.^[1] To produce such an electrode, it is necessary to have a thicker wet film containing a large quantity of solvent, which has to be removed during the drying process. This will create not only some operational difficulties, but will also affect the drying efficiency and overall production cost of LIBs. One simple way to accelerate the solvent evaporation rate is to raise the drying temperature. For example, the rate for drying a wet film containing *N*-methyl-2-pyrrolidone (NMP) solvent can increase up to 7 times from the normal drying temperature of 60 to 140 °C.^[6] However, high-temperature drying may also cause surface defects, uneven distribution of particles, binder migrations, and other heterogeneous structure problems. All of these factors may affect the electrochemical performance of the composite LIBs.^[4–14]

There have been several investigations into the effect of high-temperature drying on binder migration in electrodes. Hagiwara et al. studied the differences in binder distribution in the electrode structure between drying at 150 °C with air-

flow and under ambient condition, and observed that the particle/binder distribution in the electrode was quite uneven when dried at high temperature, with a higher concentration of binder in the upper region of the electrode.^[7] Li and Wang examined the drying behavior of different binders in aqueous and organic electrode slurries.^[8] During the constant-rate period, it took longer to dry the organic system than that in the aqueous system; thus allowing more binder to migrate upward towards the surface-coated layer. Ligneel et al. studied the drying of slurries with different solvent concentrations and found that, under the same drying conditions, binder migrated more freely towards the top surface in a concentrated solvent system.^[9,10] Buss et al. also discussed the distribution of particles and polymer dispersed in solution during drying in terms of Peclet number and sedimentation number.^[11] Indrikova et al. studied the importance of conductive network structure in an electrode plate by replacing some conductive additives with insulating ceramic particles.^[15] They found that there was a strong correlation between electronic conductivity and plate porosity with the same amount of inactive additives and network structure. Jaiser et al. studied the distribution of binding agent and conductive additives in an anode by means of energy-dispersive X-ray spectroscopy (EDS) to measure fluorine concentra-

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tions at the upper and lower surfaces of an anode.^[16] They observed that, when the sample was dried at a high drying rate, the fluorine concentration at the top surface was higher than that at the bottom surface.

To minimize binder migration, particularly in a thicker electrode used for high energy density LIBs, several approaches were tested. One was to introduce a different solvent into the drying oven to increase the vapor pressure on the electrode surface; thus reducing the solvent evaporation rate and slowing down upward binder migration.^[14] Another way was to coat two layers on a substrate sequentially by using the same slurry to achieve the designed thickness of electrode for a high-energy lithium battery.^[17] An attempt was also made by installing IR equipment between the coating die and coating film to accelerate the drying rate and suppress convection within the coating film.^[18] However, these approaches not only involved a more complicated process, but also increased the possibility of causing an explosion due to the high organic solvent concentration.

Another approach was to utilize the slot-die coating technique to produce the electrode layer. The method was invented first by Beguin for a single coating,^[19] and later extended to multilayer coating by Russell.^[20] Ruschak was the first researcher to analyze the operating window, that is, a domain for stable operations.^[21] Later, Higgins and Scriven extended Ruschak's work to include the viscous effect in the coating bead regions.^[22] Lee et al.,^[23] Carvalho and Kheshti,^[24] and Chang et al.^[25] analyzed the minimum wet thickness for slot-die coating. More detailed reviews on slot-die coating can be found in several textbooks.^[26–28]

The slot-die coating operation had been applied extensively in various optical-electronic fields. The advantage of using the slot-die coating technology to fabricate LIB electrodes is that it provides a predetermined and uniform film thickness, and can be extended to multilayer coating.^[26–33] Schmitt et al. utilized a slot-die coater to study the operating window of anode slurries for LIBs.^[29] Imachi et al. designed a two-layered cathode, with an upper layer having an enhanced energy active material, and a lower layer having a safety active material.^[30,31] Chu et al. designed a two-layered cathode with high-energy active materials to increase the discharge capacity at high C rate.^[32] Schmitt et al. extended a one-dimensional simulation method to predict the two-layered coating window by using both Newtonian and power law models, and showed that the air entrainment defect could be minimized by lowering the film thickness ratio.^[33]

Herein, a two-layered composite cathode, fabricated by using multilayer simultaneous slot-die coating technology, was proposed as an alternative to conventional single-layered cathodes used in LIBs.

Results and Discussion

The main experimental work involved making the two-layered cathodes from cathode slurries through a multilayer simultaneous slot-die coating process, followed by high-temperature drying to produce the composite cathodes. LIBs

were then assembled together with the single-layered anode and evaluated for their electrochemical performances.

Table 1 lists the compositions of the four cathode slurries formulated for the present study. The active material was $\text{Li-Ni}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ (LNMC442; Shenzhen Tianjiao Technology Co. Ltd.) of 8–12 μm average particle size. The two types of conductive agents were synthetic graphite (Timrex KS-6,

Table 1. Components of the slurries discussed herein.

Constituent [wt%]	A	B	Slurry C	D	E
LNMC442	89	89	89	89	89
KS-6	5	5	5	5	5
Super-P	2	2	2	2	2
PVDF	4	4.5	3.5	5	3
solid content	63.5	63.5	63.5	58	64.5

Timcal) of 6 μm average particle diameter, and carbon black (Super-P, Timcal) of 40 nm average particle diameter. The binder was polyvinylidene fluoride (PVDF1300, Kureha) and the solvent was NMP (Taiwan Maxwave). The major difference in these four slurries was the binder content, which varied from 3 to 5 wt%. Slurry A had a binder concentration of 4 wt%. This slurry was used to produce two single-layered structure electrodes, Cathode A-80 and Cathode B-150, for comparison purposes. The two-layered cathodes (Cathodes C and D) were produced from slurries with different binder compositions. Cathode C consisted of Slurries B and C, whereas Cathode D consisted of Slurries D and E. The overall composition of the two composite cathodes was the same as that of the single-layered electrode slurry (Slurry A).^[34] The steady shear viscosities of the five slurries were measured with an ARES-2 rheometer (TA Instrument) over a shear rate range of 0.1–1000 s^{-1} . The data in Table 2 clearly demonstrate the shear-thinning behavior of these slurries at three different shear rates.

Table 2. The viscosities of slurries at different shear rates.

Shear rate [s^{-1}]	Viscosity [Pa s]				
	Slurry A	Slurry B	Slurry C	Slurry D	Slurry E
0.1	1.77	2.27	0.99	0.77	0.81
50	1.13	1.43	0.61	0.68	0.60
100	0.99	1.31	0.56	0.67	0.57

Figure 1 a and b presents a schematic diagram and photograph of the experimental setup for the two-layered slot-die coating operation. The die was 10 cm wide, 10°, with a slot of 0.03 cm opening and a length of 1.405 cm. Both the upper and lower die pieces had the same manifold to facilitate even distribution of the coating solution issuing from the die to the moving substrate. The cathode slurries were fed separately by two pumps at the desired flow rates through each die and coated on a 20 μm aluminum substrate. The coating

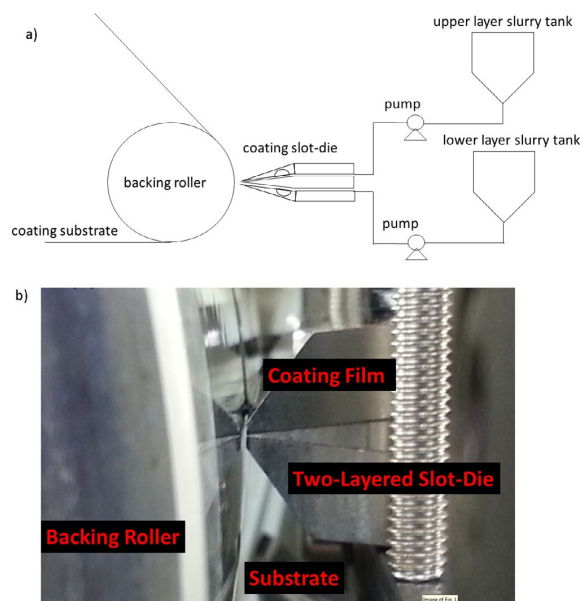


Figure 1. a) The experimental setup for the two-layered slot-die coating operation. b) Side view of the coating operation.

speed was set at 0.5 mm min^{-1} . Detailed information on the construction of the multilayer slot-die, coating device, and the operation procedure is given elsewhere.^[35] The electrode slurries were prepared according to methods presented previously.^[34,35]

Drying of the wet cathode film was performed in a two-section hot air drier, each 2 m long. The drying conditions were set at 80 and 150°C for single-layered cathodes. The two-layered composite cathodes were subjected to fast, high-temperature drying at 150°C in both sections. The final thickness of each composite cathode was around $100 \mu\text{m}$.

The penetration resistance of the dried cathode was measured by using a custom-made device, in which the sample was placed between two circular columns each of 1 cm in diameter, and subjected to a 20 kgf (1 kgf = 9.80665 N) compressive force on both ends of the column. The resistance of the electrode was measured by using a resistance instrument (Keithley 2440). The sectional structure morphology was observed by field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6500F). Analysis of energy-dispersive X-ray spectroscopy (EDS) mapping gave the fluorine composition (or binder distribution) inside the electrode. The density of the compressed dried cathode was 2.5 g cm^{-3} . The measured porosity of the electrodes was 35%.

The single-layered anode was fabricated separately by coating the anode slurry on a $15 \mu\text{m}$ copper substrate, followed by drying and compression. The active material of the anode was a mesophase graphite powder (MGP-A, China Steel Chemicals), and the conductive additive was Super-P. The binder and solvent were the same as those used in the cathode. The proportion of solid components in the anode was MGP-A/Super-P/PVDF = 94/1/5 wt%. The total solid

content of the anode slurry was 54 wt%. The slurries were coated on a $15 \mu\text{m}$ thick copper substrate performed on a R2R coater. The resulting wet anode was then dried and compressed to a set density of 1.7 g cm^{-3} .

The upper and lower layers in the film contained different compositions of binder; the upper one contained less binder than the lower one. It was thought that during the rapid high-temperature drying of the wet film, uneven binder migration would be reduced to a more uniform particle/binder network structure inside the dried composite cathode. This could provide better ionic and electronic transfer in the electrochemical reaction. A SEM-EDS mapping device was used to compare the distributions of fluorine in the two-layered composite cathodes with those of single-layered cathodes of the same formulation and composition.

Schematic diagrams of the four cathodes are shown in Figure 2; the first two represent single-layered cathodes (Cathode A-80 and Cathode B-150) and the last two represent two-layered cathodes (Cathodes C and D). Cathode A-80 was dried at 80°C ; all other cathodes were dried at 150°C . The uniformity of the film thickness of the electrodes was measured along the transverse direction (TD), taking a point every 2 cm, for a total of 5 points along one line; the average thickness was around $(100 \pm 5) \mu\text{m}$.

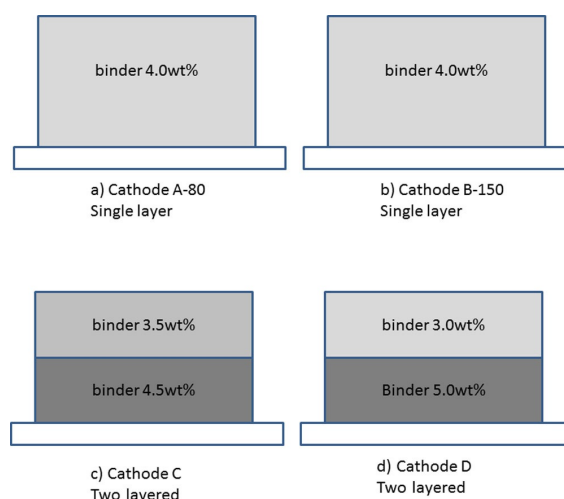


Figure 2. Schematic diagrams of the four cathodes: a) Cathode A-80, a single layer with 4.0 wt% binder dried at 80°C ; b) Cathode B-150, a single layer with 4.0 wt% binder dried at 150°C ; c) Cathode C-150, a two-layered cathode with 3.5 wt% binder in the upper layer and 4.5 wt% binder in the lower layer dried at 150°C ; d) Cathode D-150, a two-layered cathode with 3.0 wt% binder in the upper layer and 5.0 wt% binder in the lower layer dried at 150°C .

When making the two-layered cathode by means of a simultaneous multilayer slot-die coating method, the viscosities of the two cathode slurries must be compatible to maintain the minimum coating thickness to meet the design specifications.^[26–29,36] The viscosity was controlled by adjusting the solid content in each slurry, as indicated in Table 1. Under the same drying conditions, it would be more difficult for the

binding agent to move in a viscous medium due to a higher drag force.^[9,11,13] Because the two-layered cathodes (Cathodes C and D) contained different amounts of binder and solid contents in each layer, it was necessary to adjust the solid content of the slurry in each layer to match the viscosities and meet the minimum film thickness required during coating. For example, the solid contents of Slurries D and E were 58 and 64.5 wt %, respectively; the corresponding viscosities at nominal coating shear rates are given in Table 2. Two nominal shear rates of 50 and 100 s⁻¹ were selected, corresponding to low and high coating speeds of 0.5 and 1 mm min⁻¹, respectively. Because no shear force was incurred during drying, the wet film was considered to be a Newtonian slurry, with a viscosity approaching zero-shear viscosity. Hence, the viscosity value was quoted at a low shear rate of 0.1 s⁻¹.

Side views of the internal structure of the four cathode samples were observed first by SEM. Differences in the SEM images for the four samples were indistinguishable. SEM-EDS mapping analysis used by Indrikova et al. was then adopted for this study.^[15] It was a semiquantitative analytical method for elements present in a compound and showed the characteristic spectral position of an element. For example, the K α value for element F was 0.677 keV and that for element Mn was 0.637 keV. Although the relative spectral positions of the two elements were quite close, through the use of quant map analysis, the peak of each element could be further separated, and then the content could be calculated. The values of fluorine in each section indicated the binder (PVDF) distribution over the thickness of the electrode.^[15,16,37–40] Hence, the concentration of fluorine at various sections along the vertical direction of the dried cathode could be estimated.

The results in Figure 3a and b revealed that, for the two single-layered cathodes, binder migration was relatively unaf-

fected in the low-temperature drying environment (80 °C). Values of fluorine were very close throughout the entire sample thickness, but this was not the case when the samples were dried at 150 °C. The evaporation rate of solvent was influenced not only by the drying temperature, but air convection across the top surface of the electrode could also accelerate internal binder migration due to capillary forces.^[6,7,13,41] Baunach et al. found that, under high drying temperature conditions, the adhesion forces between the anode layer and substrate copper foil were relatively weak and the binder content in the region near the substrate was low.^[5] The present results on drying of cathodes at different temperatures appeared to be consistent with their observations. Conventionally, convective drying was performed in two stages: a constant rate period followed by a falling rate period. In the constant rate period, most drying occurred through the evaporation of solvent near the surface region and was controlled primarily by the drying temperature. The falling rate period was primarily a mass transfer controlled process; the removal of interior solvent due to diffusion of the solvent, as well as capillary forces from the interior to the surface of the electrode. This diffusion process may induce some upward movements of binder, resulting in a nonuniform binder distribution inside the electrode structure.^[7–9] Figure 3c and d shows the results obtained for the two-layered Cathodes C and D, in which the binder concentrations of the two cathodes were different. Cathode C (Figure 3c), which contained 3.5 wt % binder in the upper layer and 4.5 wt % binder in the lower layer, had a relatively even fluorine distribution, similar to that of Cathode A-80 (Figure 3a). This was not the case for two-layered Cathode D (Figure 3d), for which there was a significant difference in binder concentration in the two layers. Clearly, simply increasing the lower layer binder concentration could not slow down binder migration towards the electrode surface. The results obtained from EDS analy-

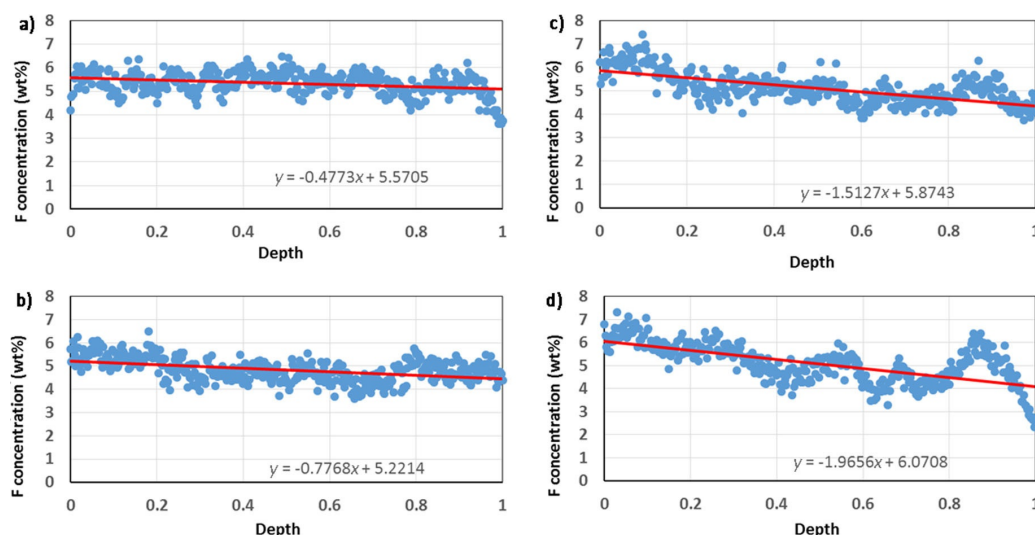


Figure 3. Fluorine analysis of the four cathodes: a) Cathode A-80; b) Cathode B-150; c) Cathode C-150; and d) Cathode D-150.

sis of fluorine concentration distribution of the dried cathode samples were consistent with that presented by Jaiser et al.^[16]

An important parameter in determining the extent of binder migration was the electrode slurry viscosity. Due to limitations of the multilayer coating device, it was not possible to coat the two layers simultaneously in equal thickness, unless the viscosities of the two slurries were similar. The viscosity of a suspension was affected by the solid content and liquid medium. To maintain a desired viscosity ratio, the compositions of the solid contents had to be adjusted accordingly. Two-layered Cathode D was made up of Slurries D and E, as shown in Figure 2d. Values of shear viscosity measured at a shear rate of 0.1 s^{-1} for these two slurries were 0.77 and 0.81 Pa s, respectively (Table 2). Significant binder migration towards the electrode surface in this cathode was found because of the low viscosity medium and high capillary forces.^[7,13,42]

The drying of wet electrodes was performed in a two-section oven of total length of 4 m. The wet electrode travelled through the oven at a speed of 1 mm min^{-1} , which gave a residence time of 4 min. The possibility of particle sedimentation during drying was considered. An estimation of settling velocity of a single particle was conducted by using the Stokes law [Eq. (1)]:

$$V_s = g(\rho_p - \rho_s)d^2 / (18\mu) \quad (1)$$

in which V_s is the settling velocity, g is the gravitational constant, ρ_p is the particle density, ρ_s is the solution density, d is the particle diameter, and μ is the nominal viscosity. Assuming a characteristic particle density of 4.0 g cm^{-3} , solution density of 1.08 g cm^{-3} , particle diameter of $12 \text{ }\mu\text{m}$, and a nominal viscosity of 0.77 Pa s (see Table 2 Slurry D, at a shear rate of 0.1 s^{-1}), a theoretical terminal velocity of $0.3 \text{ }\mu\text{m s}^{-1}$ was obtained for a single particle settling in an infinite medium. In reality, the actual settling velocity would be much lower due to additional drag forces exerted from the surrounding particles. Furthermore, the solid content and slurry viscosity would increase continuously as a result of solvent evaporation during drying. As the solid content approached its maximum packing fraction, the wet slurry would exhibit a yield stress. This would further prevent or minimize particle sedimentation. Some previous studies also reported that the LIB slurry was relatively stable with minimum particle sedimentation during coating.^[9–11,13]

The electrode resistance owing to the electrochemical reaction of the LIB was affected by the electronic conductivity of the electrode and the ionic conductivity of the electrolyte. A good electrode should have an electronic conductivity greater than that of the ionic conductivity.^[43] A penetration resistance test for each of the four cathode samples was performed to measure the plate resistance.^[31,44] The conductivity was determined from the measured plate resistance by using Equation (2):

$$\sigma = L / (RA) \quad (2)$$

in which σ is the conductivity (S cm^{-1}), L is the plate thickness (cm), R is the plate resistance (Ω), and A is the plate area (cm^2).

Because the conductivity of the active material in the cathode was relatively weak, it was necessary to add a conductive agent to the cathode slurry mixture to aid the formation of the conductive network in the structure. Although the content of the conductive additive in the four cathode samples remained unchanged, the distributions of the conductive additive and binder in the structure could vary upon drying due to differences in the slurry viscosity in each layer. Particles and binder material moved more easily in a less viscous slurry medium.^[8,12] Figure 4 shows the measured conductivities of the four samples after the drying, rolling, and pressing processes. The magnitudes of the conductivities were ordered as follows: Cathode A-80 > Cathode C > Cathode B-150 > Cathode D. Thus, under high-temperature drying conditions, the structure of Cathode C provided the best conductive network, and was expected to give the best overall battery performance among the three two-layered cathode samples.

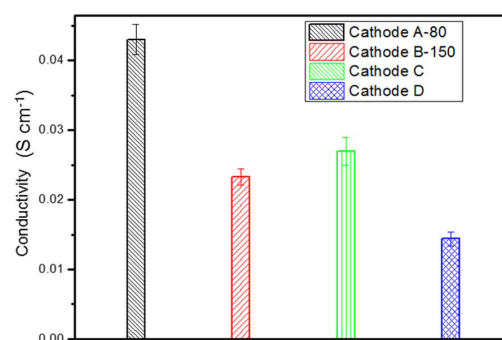


Figure 4. Values for the conductivity of the four cathodes Cathode A-80, Cathode B-150, Cathode C-150 and Cathode D-150.

The battery formation capacities with the four different cathodes are compared in Figure 5. The battery formation conditions were set by charging the battery at a fixed current density of 0.1 C and gradually increasing the voltage up to 4.2 V . The voltage was then maintained at a constant 4.2 V until the charging current dropped to less than 0.01 C . The process was repeated while keeping the current density constant at 0.1 C and letting the voltage drop from 4.2 to 3.0 V . The upper set of curves indicated that the charging capacities of the four batteries were very similar in the low to moderate voltage regions. The capacity differences became more evident in the high-voltage zone. At 4.2 V , the battery made with the two-layered Cathode C showed the highest capacity (over 140 mAh g^{-1}), followed by the one with single-layered Cathode A-80. The two batteries made with Cathodes B-150 and Cathode D reached lower capacities at the end of the charging period. A similar trend was obtained during the discharging process, as illustrated by the lower set of curves, when the voltage was reduced to 3.0 V . Of the four batteries, the ones made with Cathode C and Cathode A-80 yielded

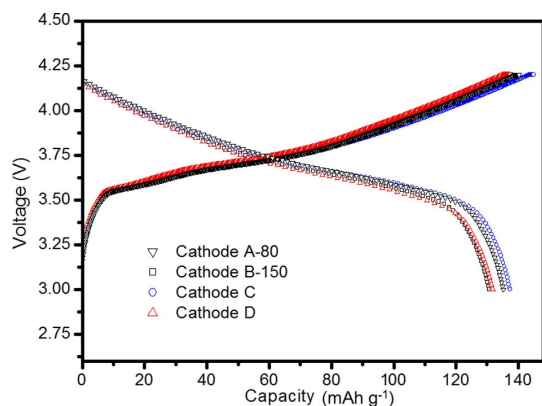


Figure 5. The battery formation capacities of the four cathodes.

a much higher capacity than the other two. Clearly, the uniformity of the conductive network in the cathode structure was an important factor that affected the battery performance. The electrochemical performance of batteries made with a better binder distribution inside the cathode structure was superior to that with a poor distribution.

Figure 6 reveals the decline in the electrical capacity of the four sample batteries at three different discharging C rates, namely, 0.2, 0.5, and 1.0 C. The battery made with Cathode A-80 was able to maintain a relatively high discharging capacity, followed by Cathode C. The two worst batteries

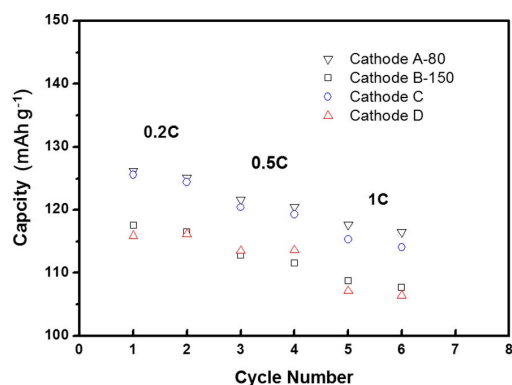


Figure 6. The battery discharging capacities of the four cathodes at different C rates.

were again those made with Cathodes B-150 and Cathode D. When the network structure was nonuniform, as in the case of Cathode B-150 and Cathode D, lithium ions would need to travel through a much longer pathway to perform the electrochemical reaction. This would result in an increase in the overall ion-transfer resistance.^[33,45–49] Consequently, the discharging capacity at varying C rates would drop more rapidly for an uneven structured battery.

Figure 7 is a similar plot depicting the discharging capacity at a rate of 1 C for the four batteries over 50 repeated cycles.

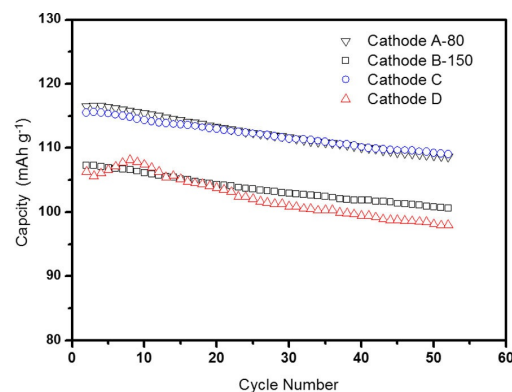


Figure 7. The battery discharging capacities at 1C rate for the four cathodes.

Again, the batteries made with Cathode A-80 and Cathode C were able to maintain a higher initial discharging capacity over a longer life cycle, whereas the other two batteries showed much faster deterioration of the discharging capacity over the same period.

Conclusions

An alternative two-layered cathode structure was designed and produced by using simultaneous multilayer slot-die coating technology to replace the conventional LIB configuration. The compositions of the cathode ingredients were varied in each layer to achieve a better binder distribution in the cathode during the high-temperature drying process. The main factor to affect the movement of coating composition, particularly the binder, was viscosity changes during drying. SEM-EDS analysis revealed that the use of a two-layered cathode of different viscosity in each layer resulted in a more uniform binder distribution in the composite cathode. A LIB electrode consisting of two-layered Cathode C and a conventional single-layered anode gave better overall electrochemical performances in terms of electrical conductivity, capacity, discharging rates, and battery life cycle.

Future work in the fabrication of two-layered cathodes for LIBs may focus on manipulating the composition of the electrode ingredients, coating thickness, and slurry viscosity ratios systematically in each layer to yield the best structural distribution for the dried two-layered cathode.

Experimental Section

Procedures for multilayer slot-die coating and subsequent drying of wet electrodes were discussed previously. The lithium battery assembly was performed in a dry room. Both cathode and anode samples were cut to sizes of 2.0×2.0 and 2.2×2.2 cm², respectively, and further dried in a vacuum oven at 120 °C for 3 h. The separator placed between the cathode and anode was a 2.5×2.5 cm² PP/PE/PP trilayer separator (Celgard 2320). An electrolyte was introduced into the dried electrodes before encapsulating the battery. The electrolyte was 1.0 M LiPF₆ dissolved in an equal volume mixture of ethylene carbonate (EC) and ethyl methyl

carbonate (EMC), together with 2.0 wt% vinylene carbonate (VC). An aluminum–plastic laminated film was used for the outer covering of the battery package.

The battery performance was examined by using a battery tester (Series-4000 Maccor). Battery formation was achieved by charging the battery at a fixed current density of 0.1 C and gradually increasing the voltage up to 4.2 V. The voltage was then maintained at a constant 4.2 V until the charging current dropped to less than 0.01 C. The process was repeated while keeping the current density constant at 0.1 C and letting the voltage drop from 4.2 to 3.0 V. The entire procedure was repeated twice to complete the battery formation process.

The electrochemical performance of the composite cathodes was tested for C rate and cycle life characteristics. The C-rate testing was performed at different discharge current densities. The procedure was similar to that of the first step of battery formation. The battery was initially charged at 0.2 C to a voltage of 4.2 V, then the voltage was held constant until the charge rate dropped to 0.01 C. The process was repeated at different C rates of 0.2, 0.5 and 1.0 C, but discharging to a voltage of 3.0 V.

The cycle life testing was performed by charging the battery at 1 C from 3.0 to 4.2 V, and then discharging from 4.2 to 3.0 V. The procedure was repeated continuously for 50 cycles.

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Keywords: binder migration • electrochemistry • layered compounds • lithium • synthesis design

- [1] D. L. Wood, J. Li, C. Daniel, *J. Power Sources* **2015**, 275, 234–242.
- [2] J. Li, C. Daniel, D. L. Wood, *J. Power Sources* **2011**, 196, 2452–2460.
- [3] J. M. Tarascon, M. Armand, *Nature* **2001**, 414, 359–367.
- [4] B. G. Westphal, H. Bockholt, T. Günther, W. Haselrieder, A. Kade, *ECS Trans.* **2015**, 64, 57–68.
- [5] M. Baunach, S. Jaiser, S. Schmelzle, H. Nirschl, P. Scharfer, W. Schabel, *Drying Technol.* **2016**, 34, 462–473.
- [6] M. Motoi, K. Ueda, A. Watanabe, K. Suda, T. Terada, K. Fujita, T. Iwade, WO2013/099569A1, **2013**.
- [7] H. Hagiwara, W. J. Suszynski, L. F. Francis, *J. Coat. Technol. Res.* **2014**, 11, 11–17.
- [8] C. C. Li, Y. W. Wang, *J. Electrochem. Soc.* **2011**, 158, A1361–A1370.
- [9] E. Ligneel, B. Lestriez, A. Hudhomme, D. Guyomard, *J. Electrochem. Soc.* **2007**, 154, A235–241.
- [10] E. Ligneel, B. Lestriez, D. Guyomard, *J. Power Sources* **2007**, 174, 716–719.
- [11] F. Buss, C. C. Roberts, K. S. Crawford, K. Peters, L. F. Francis, *J. Colloid Interface Sci.* **2011**, 359, 112–120.
- [12] C. C. Li, Y. W. Wang, *J. Power Sources* **2013**, 227, 204–210.
- [13] S. Lim, K. H. Ahn, M. Yamamura, *Langmuir* **2013**, 29, 8233–8244.
- [14] X. W. Chang, X. Q. Neo, C. Shi, T. M. Ho, CN102607240B, **2014**.
- [15] M. Indrikova, S. Grunwald, F. Golks, A. Netz, B. Westphal, A. Kwade, *J. Electrochem. Soc.* **2015**, 162, A2021–A2025.
- [16] S. Jaiser, M. Muller, M. Baunach, W. Bauer, P. Scharfer, W. Schabel, *J. Power Sources* **2016**, 318, 210–219.
- [17] N. G. Sung, D. H. Ryu, C. H. Ku, J. J. Kim, H. L. Shim, US 0224584, **2013**.
- [18] Y. Uchida, EP2424010A1, **2012**.
- [19] A. E. Beguin, U.S. Patent 2681234, **1954**.
- [20] T. A. Russell, U.S. Patent 2761791, **1956**.
- [21] K. J. Ruschak, *Chem. Eng. Sci.* **1976**, 31, 1057–1060.
- [22] B. G. Higgins, L. E. Scriven, *Chem. Eng. Sci.* **1980**, 35, 673–682.
- [23] K. Y. Lee, L. D. Liu, T. J. Liu, *Chem. Eng. Sci.* **1992**, 47, 1703–1713.
- [24] M. S. Carvalho, H. S. Khesghi, *AIChE J.* **2000**, 46, 1907–1917.
- [25] Y. R. Chang, H. M. Chang, C. F. Lin, T. J. Liu, P. Y. Wu, *J. Colloid Interface Sci.* **2007**, 308, 222–230.
- [26] E. D. Cohen, E. B. Gutoff, *Mod. Coat. Drying Technol.* **1992**, 117–167.
- [27] E. B. Gutoff, E. D. Cohen, *Coating Drying Defects* **2006**, 102–136.
- [28] S. F. Kistler, P. M. Schweizer, *Liq. Film Coat.* **1997**, 401–426.
- [29] M. Schmitt, M. Baunach, L. Wengeler, K. Peters, P. Junges, P. Scharfer, W. Schabel, *Chem. Eng. Process.* **2013**, 68, 32–37.
- [30] N. Imachi, H. Fujimoto, S. Fujitani, US 0026312, **2007**.
- [31] N. Imachi, Y. Takano, H. Fujimoto, Y. Kida, S. Fujitani, *J. Electrochem. Soc.* **2007**, 154, A412–A416.
- [32] W. B. Chu, D. J. Liu, C. C. Chen, L. C. Chen, S. T. Tseng, S. H. Wen, C. R. Yang, US 2014/0162118A1, **2014**.
- [33] M. Schmitt, S. Raupp, D. Wagner, P. Scharfer, W. Schabel, *J. Coat. Technol. Res.* **2015**, 12, 877–887.
- [34] D. J. Liu, L. C. Chen, T. J. Liu, T. Fan, E. Y. Tsou, C. Tiu, *Adv. Chem. Eng. Sci.* **2014**, 4, 515–528.
- [35] L. C. Chen, D. J. Liu, T. J. Liu, C. Tiu, C. R. Yang, W. B. Chu, C. C. Wan, *J. Energy Storage* **2016**, 5, 156–162.
- [36] Y. N. Lin, S. Y. Huang, T. J. Liu, *Polym. Eng. Sci.* **2005**, 45, 1590–1599.
- [37] A. Ponrouch, M. R. Palacin, *J. Power Sources* **2012**, 212, 233–246.
- [38] H. Ito, K. Abe, M. Ishida, A. Nakano, T. Maeda, T. Munakata, H. Nakajima, T. Kitahara, *J. Power Sources* **2014**, 248, 822–830.
- [39] S. Di Risio, N. Yan, *Colloids Surf. A* **2006**, 289, 65–74.
- [40] G. W. Lee, J. H. Ryu, W. Han, K. H. Ahn, W. M. Oh, *J. Power Sources* **2010**, 195, 6049–6054.
- [41] Y. Du, Y. H. Zang, J. Du, *Ind. Eng. Chem. Res.* **2011**, 50, 9781–9786.
- [42] C. C. Li, J. H. Jean, *Mater. Chem. Phys.* **2005**, 94, 78–86.
- [43] H. Zheng, L. Tan, G. Liu, X. Song, V. S. Battaglia, *J. Power Sources* **2012**, 208, 52–57.
- [44] W. Haselrieder, S. Ivanov, H. Y. Tran, S. Theil, L. Frobose, B. Westphal, M. W. Mehrens, A. Kwade, *Prog. Solid State Chem.* **2014**, 44, 157–174.
- [45] S. Babinec, H. Tang, A. Tailk, S. Hughes, G. Meyers, *J. Power Sources* **2007**, 174, 508–514.
- [46] G. Liu, H. Zheng, X. Song, V. S. Battaglia, *J. Electrochem. Soc.* **2012**, 159, A214–221.
- [47] D. Guy, B. Lestriez, R. Bouchet, V. Gaudefroy, D. Guyomard, *Electrochem. Solid-State Lett.* **2005**, 8, A17–A21.
- [48] N. Hatakeyama, E. Suzuki, K. Okushi, R. Mira, A. Suzuki, A. Miyamoto, *55th Battery Japan Conference*, Kyoto, Japan **2014**, **2A03**.
- [49] G. Liu, H. Zheng, A. S. Simens, A. M. Minor, X. Song, V. S. Battaglia, *J. Electrochem. Soc.* **2007**, 154, A1129–1134.

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