LiNi_{0.5}Mn_{1.5}O₄-based composite electrodes with improved properties prepared by a slurry spray deposition process

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Abstract

A slurry spray deposition (SSD) process is utilized to prepare a LiNi_{0.5}Mn_{1.5}O₄-based composite electrode supported on an aluminum foil. The spray deposition process is performed at room temperature through the atomization and deposition of the composite electrode slurry. A comparative LiNi_{0.5}Mn_{1.5}O₄-based composite electrode is also prepared by the traditional blade coating method. The surface morphology and elements mapping of the electrodes are measured by scanning electron microscopy and energy-dispersive X-ray spectroscopy, respectively. The adhesion between the composite electrode layers and the aluminum foil is also tested. A parallel evaluation on the mechanical and electrochemical performances of the two kinds of electrodes is conducted. The SSD electrode exhibits improved adhesion, cycling stability and rate capability. Therefore, the SSD process is an

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effective way to fabricate advanced electrodes for high performance lithium ion cells.

Keywords:spray deposition; blade coating; adhesion; lithium nickel manganese oxide;
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1. Introduction

Rechargeable lithium-ion batteries (LIBs) have been widely used in various portable electronics [1]. As the crucial components in determining the performance of LIBs, the electrodes (including positive and negative electrodes) are usually composites composed of active materials, conducting carbon black and polymer binders (e.g. polyvinylidene fluoride, PVDF) supported on current collectors (aluminum or copper foils). In the preparation of the active electrode materials, such as $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ [2], V_2O_5 [3], and S/C composite [4], spray drying and spray pyrolysis processes are quite effective. In addition, the spray drying process is also used to obtain better carbon coating layers in some carbon-coated active materials. For instance, $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4/\text{C}$ and LiFePO_4/C powders prepared by a spray drying process show the uniform carbon coating on the surface of $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ and LiFePO_4 particles [5, 6]. For $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$, the spherical particles synthesized with a spray drying method have higher tap density than the irregular particles prepared with an oven drying process [7].

In spite of the merits of the spray-related methods for the preparation of electrode active materials, we notice that a sintering step is needed because the precursors are in the forms of solutions or suspensions. Moreover, in order to evaporate the solvent during the spray deposition, a simultaneous drying process at an elevated temperature (usually above 200°C) is necessary. On the other hand, a blade coating or tape casting method is the state-of-the-art process to prepare the composite electrodes supported on metal foil current collectors. It is interesting to see whether the blade coating process can be replaced by a simple slurry spray deposition (SSD) method to obtain better performances of the composite electrodes.

In this work, we develop a SSD process to prepare the composite electrodes instead of the

traditional blade coating method. The active material we choose here is $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) because of its high discharge potential and energy density [8]. Although the SSD procedure is very simple, the mechanical and electrochemical properties of the thus-fabricated electrodes are improved effectively.

2. Material and methods

2.1 Preparation of the composite electrodes

Polyvinylidene fluoride (PVDF) as a binder was dissolved in the mixed solvent of N-methylpyrrolidinone (NMP) and acetone (NMP: acetone = 1:1 w/w). The addition of acetone was to accelerate the evaporation of the mixed solvent at room temperature. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO, NanomyteSP-15) was mixed with carbon black in an agate mortar and then added to the above PVDF solution to form a slurry (LNMO/carbon black/PVDF = 8/1/1 w/w/w and LNMO/NMP/acetone = 1/2/2 w/w/w). The slurry was stirred vigorously for 10h and then transferred into the tank of a high pressure spray atomizer (XIAPAI W-77). With the help of a pressurized N_2 gas at 0.2 MPa, the slurry was sprayed into tiny droplets which were deposited directly on an Al foil. The speed of deposition was $0.504 \text{ mg cm}^{-2} \text{ min}^{-1}$ (based on the mass of LNMO) and the Al foil was at room temperature. The evaporation of the NMP/acetone solvents and the deposition of the atomized droplets occurred at the same time. After the spray process, the LNMO-based electrode was transferred into an oven at 80°C and finally vacuum dried at 70°C overnight. For comparison, with a similar slurry, i.e. LNMO/carbon black/PVDF mixed in NMP (LNMO/NMP = 2/3 w/w), the blade coating method was applied to fabricate another composite electrode on an aluminum foil.

2.2 Characterization and measurement

The $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powder was evaluated by X-ray diffraction (XRD, Rigaku TTR-III) using $\text{CuK}\alpha$ radiation with a measurement range of $2\theta = 10\text{--}70^\circ$ and a step interval of 0.02° . The morphologies of the synthesized composite electrodes were observed by a scanning electron microscope (SEM, JSM-6390 LA, JEOL) and the distribution of elements was detected by energy-dispersive X-ray spectroscopy (EDX). Coin cells (2032 type) were assembled in an argon-filled glove box with the SSD-derived and the blade coated LNMO electrodes as the positive electrodes, respectively. A lithium metal foil was used as the negative electrode and 1 M LiPF_6 in 1:1 ethylene carbonate/diethyl carbonate (EC/DEC) as the electrolyte. The charge-discharge performances of the cells were characterized on a multi-channel battery test system (NewareBTS-2300, Shenzhen) with a voltage window from 3.5 to 4.9 V. Electrochemical impedance spectroscopy (EIS) measurements were also carried out on the cells with a CHI604 Electrochemical Workstation. The frequency range was from 0.01 Hz to 10^5 Hz with an applied voltage amplitude of 5 mV.

The adhesive force between the composite electrode and the Al foil was tested as following: some crossed scratches were made on the surface of the composite electrode layers with a doctor blade. These scratches formed several grids. Then an adhesive tape was used to stick on the surface of the electrode and peeled off. If the adhesion between the composite electrode layer and Al foil was not strong enough, the electrode materials would be removed away from the Al foil and stuck on the tape. Therefore, the less amount of the composite electrode layers was removed by the tape, the better its adhesion was rated.

3. Results and discussion

3.1 Characterization measurement

The XRD pattern of the LNMO powder is shown in Fig. 1. All the diffraction peaks can be indexed into a cubic spinel structure with a space group $Fd\bar{3}m$. Fig. 2 gives the top-view SEM images and EDX mappings (C and Mn elements) of the LNMO composite electrodes prepared by the blade coating (Fig. 2a, b and c) and the SSD (Fig. 2d, e and f) processes. As shown in Fig. 2a, some LNMO particles (size 2-4 μm) are covered with the nanoparticles of carbon black but some LNMO particles are barely exposed without the carbon black coating. While in Fig. 2b, most of the LNMO particles have the coverage of carbon black on the surfaces. In addition, their cross-sectional SEM images and EDX mappings (C, F and Mn elements) are given in Fig. S1. It can be seen that both of the samples show segregation to some degree. However, it seems that the distributions of C and F are less uniform in the blade coating sample compared with in the SSD sample. For the SSD sample, more F and C are detected in the region close to the Al foil, which means more PVDF binder and the conductive additive are existent in the vicinity of the foil. Therefore, the SSD process contributes to the uniform distribution by suppressing the segregation phenomenon. Such a microstructure and composition distribution are favorable for the layer adhesion and rate capability of the SSD sample, as will be confirmed below.

Figure 1 XRD pattern of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powder.

Figure 2 Top-view SEM images and EDX mappings (C and Mn elements) of the blade coating (a, b and c) and SSD samples (d, e and f).

The photo images of the samples before and after the peeling process are shown in Fig. 3. For the blade coated sample, a large piece of composite electrode was peeled off from the Al foil (Fig. 3a, b) while only very few of positive electrode film was removed from the SSD sample (Fig. 3c, d). Therefore, the composite electrode has the stronger adhesive force with the current collector for the SSD sample. The cross-sectional SEM images of the two samples are given in Fig. 4. In comparison with the blade coating sample (Fig. 4a), the interface between the composite electrode and the Al foil is more blurred for the SSD sample (Fig. 4b), suggesting a better contact on the current collector. This phenomenon is consistent with the results of scratch test in Fig. 3. Hence, there seems more uniform distribution of the binder out of the spray deposition process.

Figure 3 Photo images of scratch test of the blade coating (a, b) and SSD samples (c, d).

Based on above results of the more uniform carbon black distribution, it may be concluded that the SSD process can result in more uniform distribution of the slurry components on the composite electrode layers. This can be explained by the possible partial segregation phenomenon in the blade coating process. After the slurry is coated on the Al foil, a certain degree of segregation of the slurry components (LNMO, carbon black and PVDF) may take place along with the relatively slow drying step. For instance, the lighter PVDF may tend to stay a little far away from the Al support than the heavier LNMO particles, which can cause the relatively poor contact at the interface between Al foil and the composite electrode. On the other hand, for the SSD process, the droplets are forced to land on the Al foil by the pressurized N_2 so that a good contact is secured initially. Furthermore, the evaporation of the solvents (including acetone) of the sprayed slurry is faster than in the blade coating process so that the degree of possible segregation of the components should be much less for the spray deposition. Therefore, the homogeneity of the components in the SSD sample is better than in

the blade coating sample, as evidenced by the results of the above SEM analyses and scratch test.

It should be noted that acetone plays an important role in the SSD process because its much faster vaporization than NMP helps to suppress the segregation phenomenon. In the scratch test, an SSD composite electrode prepared with a slurry without acetone shows a weak adhesion with Al foil (see supplementary materials, Fig. S2). Moreover, for the blade coating process, the addition of acetone can also improve the adhesion to some degree. However, the use of NMP/acetone mixed solvent in the slurry does not improve the distribution of carbon black in the blade coating sample. For the SSD process, the slow evaporation of NMP results in more segregation because the heavier LNMO particles are observed to lie under the lighter carbon and PVDF components (see supplementary materials, Fig. S3).

Figure 4 Cross-sectional SEM images of the blade coating (a) and SSD (b) composite cathode films on Al foil.

3.2 Electrochemical performances measurement

The LNMO mass loading of the blade coating sample is 2.60 mg cm^{-2} with a layer thickness of $64.8 \text{ }\mu\text{m}$, while the LNMO mass loading of the SSD sample is 2.52 mg cm^{-2} with a layer thickness of $64.0 \text{ }\mu\text{m}$. Thus, the densities of blade coating and SSD samples can be calculated as 4.01 g cm^{-3} and 3.94 g cm^{-3} , respectively. Fig. 5a shows the voltage profiles of

the blade coating and the SSD samples tested by galvanostatically charging/discharging the Li/LNMO cells at 0.5 C rate (1 C = 120 mA g⁻¹ (equivalent to a current density of 0.30 mA cm⁻²)) at room temperature. Both cells deliver a capacity of 132 mAh g⁻¹ but a slightly smaller polarization can be observed for the SSD sample. Additionally, both samples show a small plateau at about 4.0 V, whose length is related to the Mn³⁺ content [9]. The cycling performances of the cells are shown in Fig. 5b. The SSD sample keeps a capacity retention of 97.9% after 125 cycles, which is higher than 89.8% obtained for the blade coating sample. The improvement in the cycling stability for the SSD sample is attributed to the less polarization and better electrode adhesion thanks to the special microstructure obtained by this preparation technique.

Figure 5 Charge-discharge characteristics (a) and cycling performances (b) of the blade coating and SSD samples. The cells are charged/discharged at 0.5 C and 1 C for five times, respectively, in the first 10 cycles then at 2 C in the following cycles.

To compare the polarization of both cells, the electrochemical impedance spectra of the blade coating and SSD samples at the 125th cycle are shown in Fig. 6. The equivalent circuit and the fitted results are also given in the figure. Each spectrum consists of a semicircle in the high frequency range and a sloping line in the low frequency range. The intercept at the real

axis at the high frequency end is related to the ohmic resistance of the electrolyte solution (R_e). The semicircle is related to the charge transfer process at the interface between the electrolyte solution and the LNMO electrode (R_{ct} and CPE_1), while the sloping straight line in the low frequency range reflects the lithium ion diffusion in the electrodes (CPE_2). It is found that the fitted R_e values after cycling are similar for both samples. However, the fitted R_{ct} value for the SSD sample is smaller than that of the blade coating one, indicating a faster charge transfer process for the cell with the SSD LNMO electrode as the cathode. This is resulted from the more uniform distribution of carbon black of the SSD sample, which forms a better electron conducting network and hence faster charge-transfer process. It also means the electrochemical reactions at the interface between the electrolyte and the electrode proceed faster.

Figure 6 Electrochemical impedance spectra of the blade coating and SSD samples.

The rate capability characteristics of both cells are shown in Fig. 7. The spray deposited sample delivers discharge capacities of 126.0 and 123.5 mAh g⁻¹ at the C-rates of 8C and 10 C,

whereas the blade coating sample exhibits discharge capacities of only 115.4 and 103.0 mAh g⁻¹ at the same C-rates. It is obvious that the SSD method can enhance the electronic conductivity of the electrode, which leads to better rate capability. With the increase of current density, the decrease in the capacity is strongly related to the electrochemical polarization. As shown in Fig. 7b and c, the two samples suffer different degrees of polarization. At 10 C rate, the blade coating sample gives a sloping discharge profile with an average discharge voltage of 4.0 V, while the SSD sample still shows an obvious discharge plateau at 4.45 V. Compared with the blade coating sample prepared with a slurry with NMP/acetone mixed solvent and the SSD sample prepared with a slurry with pure NMP as solvent (Fig. S4), it is confirmed that above optimized SSD sample exhibits the best rate performances.

Figure 7 Discharge capacities of the blade coating and SSD samples (a) at different rates and

the discharge profiles of the blade coating (b) and SSD (c) samples.

4. Conclusions

In conclusion, the slurry spray deposition (SSD) process at room temperature is investigated as a possible substitute for the widely used blade coating method to fabricate composite electrodes for rechargeable lithium-ion batteries. The advantages of the SSD lie in the easy manipulation and the possibility in large scale application for various electrode materials. Despite of its simple procedures, the mechanical and electrochemical properties of the composite electrodes are improved effectively.

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Figures captions:

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