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Experimental Study on Performance Improvement of Lithium Nickel Manganate High Voltage Cathode Material

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Abstract. The development of high-voltage electrolyte system is a key factor in the commercialization of high-voltage spinel lithium nickel manganese oxide (LNMO) battery materials. This article carries out the optimization and exploration of LiBOB electrolyte additives in high voltage LNMO cathode materials. The test results show that the performance is best when the electrolyte is added at 30-50 μL. In order to study the mechanism of LiBOB on the LNMO anode, combining the characterization results of XRD, XPS, IR, Raman, and electron microscopy, it can be seen that LiBOB is preferentially oxidized and a layer of boron-rich CEI film with a thickness of about 8 nm is formed on the surface of the LNMO anode. This passivation film physically blocks the contact between the electrolyte and the surface of the highly active electrode, maintains the stability of the LNMO structure under high voltage, and improves the electrochemical performance.

Keywords. Power battery, lithium nickel manganese oxide, high voltage cathode, cycle performance, LiBOB electrolyte additive

1. Introduction

The cathode material is the core component that determines the cycle performance and safety performance of lithium-ion batteries. In order to further improve the energy density of batteries, the research and development of high-voltage cathode materials is imperative [1]. Among them, lithium nickel manganese oxide (LNMO) materials with stable spinel structure have a charging voltage of 5 V and a theoretical capacity of 147 mAh g^{-1}, and contain only two transition metal elements nickel and manganese, which are rich in resources [2]. It is considered to be a high-voltage cathode material with great development potential. The research on LNMO materials at home and abroad shows a momentum of rapid growth, but LNMO has not achieved real commercialization [3~4]. The biggest dilemma on the road to mass production is the inability to find electrolytes on the market that can withstand such high voltages. When the charging voltage exceeds 4.3 V, the ordinary carbonate type electrolyte will undergo irreversible oxidation and decomposition, accompanied by severe interface side reactions, making the battery performance unable to meet the expectations [5]. Therefore, it is particularly important to optimize the electrolyte to improve its withstand voltage for the further promotion of high voltage cathode materials.

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In this paper, high voltage LNMO was used as the positive electrode, and 1.0 M LiPF6 EC/EMC (4/6 wt%) was used as the original electrolyte. Firstly, the appropriate amount of electrolyte was explored. Then LiBOB was selected as an additive to explore the optimal concentration of LiBOB in LNMO system.

2. Experimental Method

2.1. Electrolyte Configuration

Commercial 1.0 M LiPF6 EC/EMC (4/6 wt%) was selected as the original electrolyte. Before using LiBOB, bake it for 10 hours under 80 °C vacuum atmosphere. Then accurately weigh LiBOB with the calculated mass in advance in the glove box with an electronic balance, pour it into the original electrolyte and shake it until it is evenly mixed to prepare the electrolyte containing 0.01, 0.05, 0.1, 0.2, 0.3 and 0.4 M LiBOB.

2.2. Testing and Characterization

The coating of LNMO and NCM811 cathode materials, electrode preparation, battery assembly process, relevant electrochemical tests and electrode physical characterization methods are carried out as described in Chapter 2.

2.3. Conductivity Test

The conductivity of the original electrolyte and the electrolyte containing 0.1 M LiBOB were tested by using the magnetic DDS-307A conductivity tester. Use 1.0 M KCl standard solution to correct the conductivity of the instrument. When testing the conductivity, use the temperature probe to ensure that the measured sample is tested at the same temperature.

3. Results and Discussion

3.1. Optimization of Electrolyte Injection Volume

It is particularly important to determine the appropriate amount of electrolyte for the balance between performance and cost of lithium-ion batteries. The amount of electrolyte required by different cathode materials is different. It is generally believed that lithium cobalt oxide needs less electrolyte, while ternary and lithium manganate materials need more electrolyte, which is mainly related to their compaction density.

The 1.0 M LiPF6 EC/EMC (4/6 wt%) original electrolyte was selected to optimize the injection amount. The cyclic voltammetry (CV) curve of the electrolyte reflected the oxidation degree of the electrolyte. Firstly, 30, 50, 80 and 120 μL of electrolyte were added to a cell with metal lithium metal as reference and counter electrode and stainless steel spacer as working electrode and the oxidation performance of electrolyte was tested in the interval from open circuit voltage to 5 V with a sweep rate of 0.5 mV s^{-1}. As shown in figure 1(a), the injection volume is 120 μL oxidation current(>20 μA) much higher than other injection volumes (<10 μL), 80 μL oxidation current is less than 120 µL, but more than 30µL and 50 µL. The analysis of figure 1(a) shows that when too much electrolyte is added, it will be oxidized and decomposed in large quantities, causing unnecessary consumption, so the injection amount should be less than 80 µL. Figure 1(b) shows the first charge discharge curve (voltage range 3.0-4.9 V) of LNMO batteries with different electrolyte quantities at 0.1 C rate. Table 1 shows the corresponding capacity and coulomb efficiency.

Table 1. First cycle charge discharge capacity and coulomb efficiency of LNMO under different electrolyte injection amounts.

Injection volume/ µ L	**Charge specific capacity /mAh g^{-1}**	**Discharge specific capacity/mAh g^{-1}**	**Coulomb efficiency/%**
20	148.6	126.1	84.88
30	150.1	127.6	84.99
50	151.1	124.7	82.49
80	150.9	126.0	83.53
100	156.3	125.1	80.04
120	156.9	128.8	82.11

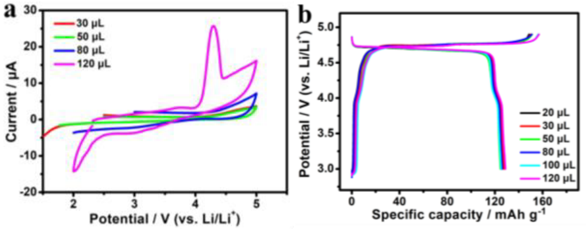

Figure 1. (a) Cyclic voltammetry curve of stainless steel/li battery with different electrolyte injection amount. **(b)** first cycle charge discharge curve of LNMO in different electrolyte amount.

Figure 2(a) shows the impedance curve of LNMO in discharge state after two cycles of activation at 0.1 C. When the dosage exceeds 80 µL, excessive electrolyte decomposition deposition led to the thickening of CEI film on the positive surface, and the corresponding interface impedance (the part represented by the semicircle) increased significantly. As shown in figure 2(b), when the electrolyte is too small, it is not conducive to the battery capacity (20 µL of 300 turn specific capacity 58.1 mAh g^{-1} less than 50 µL of 73.2 mAh g^{-1}).

The electrolyte range of 20 to 80 µL is too wide. In order to obtain a more accurate addition, we took points at 10 µL intervals between 20-80 µL and tested their CV curves separately. Figure 3(a) shows Minimum oxidation current at 30 µL, the current is obviously larger when 70 µL is added. Further analysis of the first cycle charge and discharge data of LNMO in table 2, we shows that the charging capacity of the first cycle under 70 µL is 160mAhg^{-1}, and the coulomb efficiency is only 74.76%. It is generally believed that the loss of the first turn capacity is closely related to the decomposition of electrolyte and the stability of interface, so it is concluded that 70 µL electrolyte is still excessive (figure 3b).

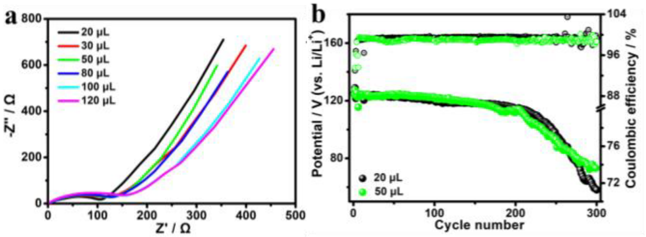

Figure 2. (a) Impedance curve of LNMO in discharge state after 0.1C activation for two cycles in different electrolyte dosage. **(b)** Cycle curve of LNMO battery in 20 μL electrolyte.

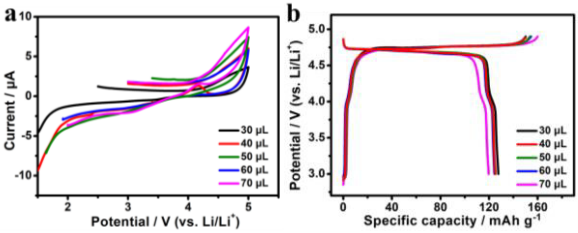

Figure 3. (a) CV Curve of stainless steel/Li battery with 30/40/50/60/70 μL electrolyte volume. **(b)** first cycle charge discharge curve of LNMO at corresponding injection volume.

Table 2. First turn specific capacity and coulomb efficiency of LNMO in different electrolyte quantities.

Injection volume/ μL	**Charge specific capacity /mAh g^{-1}**	**Discharge specific capacity/mAh g^{-1}**	**Coulomb efficiency/%**
20	148.6	126.1	84.88
30	150.1	127.6	84.99
50	151.1	124.7	82.49
80	150.9	126.0	83.53
100	156.3	125.1	80.04
120	156.9	128.8	82.11

Considering the influence of different electrolyte additions on the polarization degree of LNMO/Li battery, we conducted the CV test as shown in figure 4, with a scan speed of 0.1 mV s^{-1}. LNMO material contains two kinds of transition metal ions, of which Ni element is the active component providing capacity, corresponding to two oxidation peaks of about 4.7 V, and the oxidation of Mn element corresponds to a small peak at 4.0 V, and the oxidation-reduction peaks of the two elements have corresponding platforms in the charge discharge curve. As shown in figure 4, the shape of CV Curve under different dosage is basically the same, but compared to that of 30 and 50 μL, the peak potential at 4.7 V of the first cycle under 60 μL deviates from that of the second and third cycles.

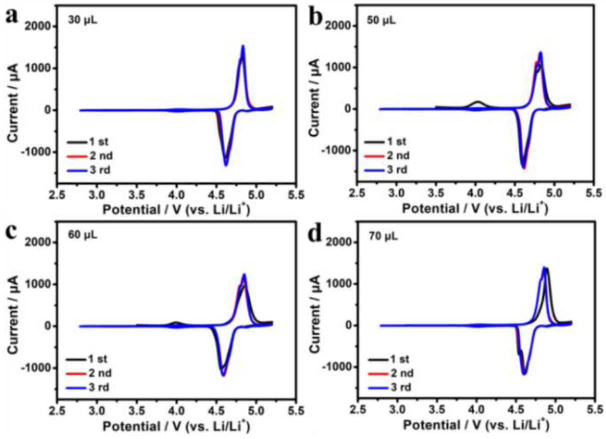

Figure 4. CV Curve of LNMO/Li half cell under different electrolyte quantities.

In order to further prove the influence of appropriate electrolyte on electrode materials and battery performance, we carried out a group of control experiments: adding 10, 50, 120 μL electrolyte for the LNMO battery, cycle 200 cycles at 1C rate, then disassemble the battery, take out the positive electrode, and take optical photos of the corresponding diaphragm. After that, the cathode was reassembled into electrolyte with the amount of 10, 50 and 120 μL of battery, continue to cycle for 100 cycles, and get the cycle curve in figure 5(a).Capacity decay in the first 200 weeks of cycling for cells with 120 μL electrolyte volume. Figures 5(b-d) show a picture of the diaphragm in the battery after 200 cycles with different amount of electrolyte.

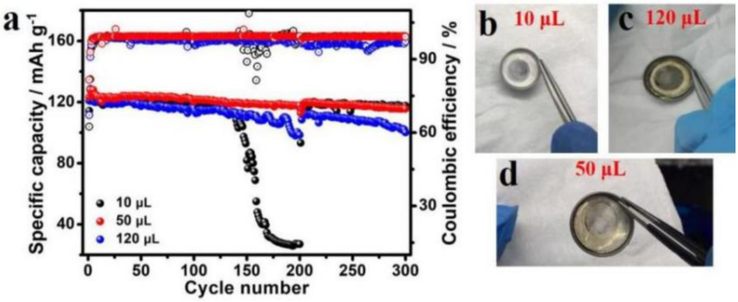

Figure 5. (a) Cycle performance curve for LNMO at 10, 50 and 120 μL electrolyte additions. **(b-d)** optical photos of diaphragm after 200 cycles with 10, 50 and 120 μL electrolyte additions.

3.2. Optimization of LiBOB Dosage

The appropriate proportion of electrolyte additives will have the best modification effect on the positive surface. In order to explore the reasonable ratio of LiBOB additives, LiBOB of 0.01, 0.05, 0.1 and 0.4 M were added to the original electrolyte respectively, and the CV test was carried out on the distributed hydrolysate. The sweep speed was 0.1 mV s^{-1}, and the voltage range was 3.0-5.0 V (vs. li/li+, figure 6a). Figure 6(b) shows the first cycle charge discharge curve of LNMO/Li battery in electrolyte containing different LiBOB. The first cycle coulomb efficiency was only 78.60%, lower than 82.49% in the original electrolyte, which indicating that too much LiBOB dissociation results in a large irreversible capacity loss during the first cycle charging process. There is little difference in the first cycle charge discharge curve when the LiBOB dosage is 0.01, 0.05 and 0.1 M. So the LiBOB dosage should be less than 0.4 M.

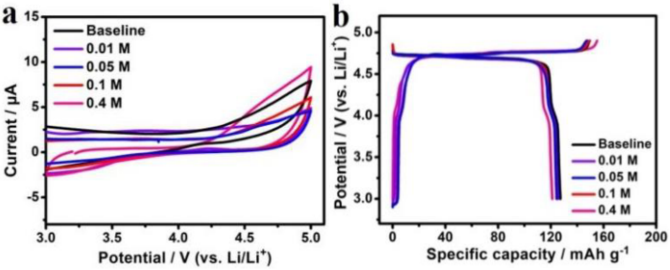

Figure 6. (a) Electrolyte oxidation curve under different LiBOB dosage. **(b)** first turn voltage capacity curve of corresponding LNMO battery.

4. Conclusion

This paper focuses on the optimization and exploration of LiBOB electrolyte additive in high voltage LNMO cathode material. Relevant contents are summarized as follows:

(1) The amount of electrolyte are optimized. On the basis of lithium hexafluorophosphate+vinyl carbonate/methyl ethyl carbonate ($LiPF_6$+EC/EMC) electrolyte, the cyclic voltammetry curve, interface impedance, first cycle charge discharge and long cycle performance of the battery were compared under different electrolyte injection amounts. The results showed that the high voltage LNMO cathode can give full play to its capacity without excessive interface side reactions when the electrolyte injection amount ranged from 30 to 50 μL.

(2) Considering the inevitable electrolyte consumption during the battery cycle, in order to prolong the service life of the battery as much as possible, 50 μL is used as the amount of electrolyte added in subsequent experiments.

(3) The appropriate proportion of LiBOB in the original electrolyte was adjusted with LNMO as the cathode. The electrolyte with different content of LiBOB was cyclic tested. It was found that when the LiBOB content was 0.1 M, the LNMO cathode showed excellent performance at room temperature and high temperature.

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