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Electrochemical Performance Test of Lithium Manganese Oxide - Test Method for Discharge Plateau Capacity Ratio and Cycle Life

锰酸锂电化学性能测试

放电平台容量比率及循环寿命测试方法

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Electrochemical Performance Test of Lithium Manganese Oxide - Test Method for Discharge Plateau Capacity Ratio and Cycle Life

1 Scope

This Standard specifies the test method for discharge plateau capacity ratio and cycle life of lithium manganese oxide as the cathode material of lithium ion batteries.

This Standard is applicable to the test of discharge plateau capacity ratio and cycle life of lithium manganese oxide as the cathode material of lithium ion batteries.

2 Normative References

The content in the following document constitutes indispensable clauses of this document through normative references in the text. In terms of references with a specified date, only versions with a specified date are applicable to this document. In terms of references without a specified date, the latest version (including all the modifications) is applicable to this document.

GB/T 18287 General Specification of Lithium-ion Cells and Batteries for Mobile Phone

3 Terms and Definitions

The following terms and definitions are applicable to this document.

3.1 Solid Content

Solid content refers to the mass fraction (of the total amount) of the remaining part of emulsion or paint after drying under the specified conditions.

4 Test Conditions

When there are no special instructions, the various test procedures specified in this document should be carried out in a drying room (the environmental dew-point temperature is ≤ -20 °C). For the situation where there is no drying room, the various test procedures shall be carried out under the following environmental conditions: the relative humidity is ≤ 20.0% and the temperature is 20 °C ~ 30 °C.

160 μm; the thickness of the aluminum foil coated on the surface of the aluminum-plastic film is: 30 μm ~ 40 μm.

5.17 Insulating glue: with a length of 53.0 mm ± 1.0 mm.

5.18 Nitrogen: purity (volume fraction) ≥ 99.9%.

5.19 Electrolyte for lithium ion batteries: composed of a solution (with a concentration of 1 mol/L) of lithium hexafluorophosphate ($LiPF_6$) dissolved in an organic solvent (the volume ratio of ethylene carbonate EC, dimethyl carbonate DMC, ethyl methyl carbonate EMC is 1 : 1 : 1); moisture content ≤ 0.0015%; free acid (HF) ≤ 0.003%; density: 1.23 g/cm^3 ± 0.02 g/cm^3; chroma ≤ 50 Hazen.

6 Instruments and Equipment

6.1 Electronic balance: with a measuring range of 3,000 g and a division value of 0.01 g.

6.2 Electronic balance: with a measuring range of 100 g and a division value of 0.0001 g.

6.3 Drying oven.

6.4 Desiccator.

6.5 Sanding machine.

6.6 Planetary stirrer.

6.7 Coating machine: the length of drying tunnel is > 2.0 m.

6.8 Vacuum oven.

6.9 Cutting machine.

6.10 Banister brush.

6.11 Adjustable slitting machine.

6.12 Sheet-punching machine: the mold is a square with a side length of 10 cm or a circle with a diameter of 10 cm.

6.13 Desktop digital thickness gauge: with a resolution of 1 μm.

6.14 Roller machine: exclusive to lithium batteries.

6.15 Ruler: stainless-steel; with a measuring range of 100 cm, accurate to 0.5 mm.

Add the weighed NMP (5.4) into the stirring tank in the sanding machine (6.5); gradually add the weighed polyvinylidene fluoride (5.3) and perform dispersive stirring, until it is completely dissolved. Afterwards, add the weighed conductive agent (5.2) and perform dispersive stirring. After the dispersion is uniform, add the weighed lithium manganese oxide (5.1) and perform dispersive stirring, until the dispersion is uniform.

7.2.3 Coating

Use the coating machine (6.7) to evenly coat the stirred cathode paste on both sides of the aluminum foil (5.5). The coating speed parameter of the coating machine (6.7) is set to 800 mm/min; the blast baking temperature is set to 130 °C. Control the single surface areal density within the range of 200 g/m^2 ~ 230 g/m^2, the thickness difference ≤ 3 μm and the areal density deviation of the front and back surfaces < 5.0 g/m^2. After the coating is completed, transfer the preliminarily dried and winded cathode sheet to the vacuum oven (6.8) for secondary drying. The baking temperature is controlled at 110 °C ~ 120 °C; bake for 12 h; cool down under nitrogen (5.18) atmosphere.

7.2.4 Preparation

Take the cathode sheet in 7.2.3, which is dried and reaches the requirements of being processed; use the sheet-punching machine (6.12) to punch out a circular or square cathode sheet with an area of S_c. Use the electronic balance (6.2) and the desktop digital thickness gauge (6.13) to perform mass measurement m_c and thickness measurement d_c on the punched cathode sheet.

Use the sheet-punching machine (6.12) to punch out an aluminum foil substrate with an area of S_c. Use the electronic balance (6.2) and the desktop digital thickness gauge (6.13) to perform mass measurement m_{Al} and thickness measurement d_{Al} on the punched aluminum foil substrate.

The compaction density ρ_c of the cathode sheet shall be calculated in accordance with Formula (1):

$$\rho_c = \frac{m_c - m_{Al}}{S_c \times (d_c - d_{Al})} \times 10^4 \quad \cdots\cdots (1)$$

Where,

ρ_c---the compaction density of the cathode sheet, expressed in (g/cm^3);

m_c---the mass of the cathode sheet, expressed in (g);

m_{Al}---the mass of the aluminum foil substrate, expressed in (g);

S_c---the area of the cathode sheet, expressed in (cm^2);

d_c---the thickness of the cathode sheet, expressed in (μm);

graphite anode (5.9), conductive agent (5.2), sodium carboxymethyl cellulose (5.10) and styrene butadiene rubber emulsion (5.11); use the electronic balance (6.1) for weighing. In accordance with the solid content of 50.0% ~ 60.0%, calculate deionized water (5.12); use the electronic balance (6.1) for weighing.

7.3.2 Pulping

Add the weighed deionized water (5.12) into the stirring tank in the planetary stirrer (6.6); gradually add the weighed sodium carboxymethyl cellulose (5.10) and perform dispersive stirring for over 2 h, until it is uniform. Add the weighed conductive agent (5.2) and perform dispersive stirring, until the dispersion is uniform. Add the weighed artificial graphite anode (5.9) and perform dispersive stirring. Finally, add the weighed styrene butadiene rubber emulsion (5.11) and perform dispersive stirring, until the dispersion is uniform.

7.3.3 Coating

In accordance with the areal capacity of the anode sheet: when the areal capacity of the cathode sheet is ≥ 1.1, calculate the single surface areal density of the anode sheet; control the areal density deviation of the front and back surfaces < 5.0 g/cm^2.

Use the coating machine (6.7) to evenly coat the 7.3.2 stirred anode paste on both sides of the copper foil (5.13). The coating speed parameter of the coating machine (6.7) is set to 800 mm/min; the blast baking temperature is set to 90 °C.

After the coating is completed, transfer the preliminarily dried and winded anode sheet to the vacuum oven (6.8) for secondary drying. The baking temperature is controlled at 100 °C ~ 110 °C; bake for 12 h; cool down under nitrogen (5.18) atmosphere.

7.3.4 Preparation

Take the anode sheet in 7.3.3, which is dried and reaches the requirements of being processed; use the sheet-punching machine (6.12) to punch out a circular or square anode sheet with an area of S_a. Use the electronic balance (6.2) and the desktop digital thickness gauge (6.13) to perform mass measurement m_a and thickness measurement d_a on the punched anode sheet.

Use the sheet-punching machine (6.12) to punch out a copper foil substrate with an area of S_a. Use the electronic balance (6.2) and the desktop digital thickness gauge (6.13) to perform mass measurement m_{Cu} and thickness measurement d_{Cu} on the punched copper foil substrate.

The compaction density ρ_a of the anode sheet shall be calculated in accordance with Formula (2):

$$\rho_a = \frac{m_a - m_{Cu}}{S_a \times (d_a - d_{Cu})} \times 10^4 \qquad \cdots\cdots (2)$$

c) Take the cathode sheet in 7.2.4 and place it on the above-mentioned half-folded separator; align the cathode sheet, the separator and the anode sheet in the center; make the active substance coverage area of the cathode sheet completely aligned with the active substance coverage area of the anode sheet, and then, perform winding;

d) Take out the winding core, which is winded in a certain shape, from the winding needle. Use the insulating glue (5.17) to paste the tail of the winding core and the battery body together;

e) Place the winding core flatwise on the battery flat press (6.17) to press and level it;

f) Number and record the leveled winding cores one by one; place them in the vacuum oven (6.8); set the oven temperature to 80 °C; vacuumize and dry for 24 h. During the baking process, in every 4 h, vacuumize and supplement nitrogen once;

g) Use the aluminum-plastic film heat sealing machine (6.18) to seal the pack the winding core in the aluminum-plastic film (5.16), with an air bag and liquid injection tube (6.21) on one side;

h) Place the plastic-sealed battery in the drying oven (6.3) and bake it for 10 h. Set the oven temperature to 80 °C. After baking, transfer it to the inert atmosphere (argon) glove box (6.20). At the air bag of the battery, use the liquid injector (6.22) to inject the electrolyte for lithium ion batteries (5.19) into the liquid injection tube (6.21); use the insulating glue (5.17) to seal it;

i) Place the test battery (with the air bag facing upwards) with the injected electrolyte for lithium ion batteries (5.19) aside for 24 h ~ 36 h.

7.6 Battery Formation

Take the test battery, which is placed aside in 7.5; place it in insulating splints; use an appropriate mode to fix it. Afterwards, place the test battery with the insulating splints into the thermostat (6.23). Set the thermostat temperature to 45 °C ± 1 °C; preserve the heat for 2 h ~ 3 h.

Use the lithium-ion battery electrochemical performance testing machine (6.24) for charging and discharging. The charging and discharging system is as follows:

a) Charging cut-off voltage: 4.20 V;

b) Discharging cut-off voltage: 3.00 V;

In the first cycle, charge in accordance with the requirements: 0.02 C for 4 h, 0.05 C for 4 h, 0.1 C for 2 h, and 0.2 C, until it reaches the cut-off voltage; perform constantvoltage in the n^{th} cycle is recorded as Q_n.

8 Test Data Processing

8.1 Calculation of Discharge Plateau Capacity Ratio

The discharge plateau capacity ratio in the n^{th} cycle of lithium manganese oxide is calculated in accordance with Formula (4):

$$P_n = \frac{Q_{n,U}}{Q_n} \times 100\% \qquad \cdots\cdots\cdots (4)$$

Where,

P_n---the discharge plateau capacity ratio in the n^{th} cycle;

$Q_{n.U}$---the discharge capacity when discharged to the voltage U (3.60 V) requested by the test in the n^{th} cycle, expressed in (mA • h);

Q_n---the discharge capacity when discharged to the cut-off voltage in the n^{th} cycle, expressed in (mA • h).

The calculation result shall retain one decimal place.

8.2 Calculation of Cycle Life

The ratio of the discharge capacity of lithium manganese oxide in the n^{th} cycle to the discharge capacity in the first cycle is calculated in accordance with Formula (5):

$$\eta_n = \frac{Q_n}{Q_1} \times 100\% \qquad \cdots\cdots\cdots (5)$$

Where,

η_n---the ratio of the discharge capacity in the n^{th} cycle to the discharge capacity in the first cycle;

Q_n---the discharge capacity in the n^{th} cycle, expressed in (mA • h);

Q_1---the discharge capacity in the first cycle, expressed in (mA • h).

The cycle life of lithium manganese oxide shall be determined in accordance with the following method: when $\eta_n \geq 80\%$, $\eta_{n+1} < 80\%$, the number of cycles (n) is the cycle life of the test sample.

------ The End ------