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GB/T 44027.1-2024

Determination method of carbon material - Part 1: Determination of first discharge specific capacity, first coulombic efficiency, discharge capacity retention rate at different rates

炭材料测定方法 第1部分:首次放电比容量、首次库仑效率、不同倍率放电容量保持率的测定

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Note Note on the printed English title

The English title printed on the cover of the document reads first columbic efficiency. The word is a misprint for coulombic, which is the term used throughout the field and the one that matches the Chinese wording of the title, and it is given here as first coulombic efficiency. Nothing else in the printed title has been changed.

1 Scope

The document describes the reagents and materials, the instruments and equipment, the test procedure, the calculation of results and the treatment of data, and the test report for the determination, on a coin type half cell, of the first discharge specific capacity, the first coulombic efficiency and the discharge capacity retention rate at different rates of carbon negative electrode materials for lithium-ion batteries.

It applies to the determination of those three properties on artificial graphite, natural graphite, carbon composite silicon monoxide and silicon carbon negative electrode materials for lithium-ion batteries. The normative references are GB/T 4369 on lithium and GB/T 8170 on rounding. The document defines no terms of its own.

This is the first part of GB/T 44027. The introduction states that the series is planned in

three parts: part 1 on the three properties above, part 2 on the expansion ratio of the coating, and part 3 on the fluff content of carbon materials.

4 Reagents and materials

Conductive carbon black has an ash content of not more than 0.05 %, a moisture content of not more than 0.1 %, a specific surface area of 50 m2/g to 80 m2/g and a median particle size D50 of 30 nm to 60 nm. Conductive graphite has the same ash and moisture limits and a median particle size D50 of 100 nm to 300 nm.

The acrylonitrile multi-copolymer has a viscosity above 7300 mPa.s measured at 25 °C on a 1 % solids solution and a median particle size D50 of not more than 1 micrometre. Sodium carboxymethyl cellulose has a viscosity of 3000 mPa.s to 5000 mPa.s under the same conditions and a pH of 6.0 to 8.5. Styrene butadiene rubber has a pH of 5.0 to 7.5 and a median particle size D50 of 150 nm to 220 nm.

The lithium foil or strip meets grade Li-3 of GB/T 4369, with a diameter of 16 mm to 19 mm and a thickness of 0.5 mm to 1.2 mm. The copper foil has a thickness given in the document as 7 mm to 15 mm. The nickel foam has a diameter of 14 mm to 19 mm and a thickness of 0.15 mm to 0.25 mm, and the separator is a polyethylene and polypropylene composite film of 18 mm to 20 mm diameter.

The electrolyte is lithium hexafluorophosphate dissolved at 1 mol/L in an organic solvent of ethylene carbonate, dimethyl carbonate and ethyl methyl carbonate in the volume ratio 1 to 1 to 1. The coin cell components are the standard structural parts of a CR2016 or CR2032 cell: negative case, spacer, spring support plate, which the CR2016 does not include, and positive case.

5 Instruments and equipment

The battery tester has a current accuracy and a voltage accuracy of 0.05 % of reading plus 0.05 % of full scale. The inert atmosphere argon glove box works at one standard atmosphere with a total leak rate of the box, as volume fraction, of not more than 5 x 10-4 per hour.

The vacuum drying oven reaches a vacuum below 100 Pa over a control range from room temperature to 250 °C, with a maximum temperature fluctuation of +/-2 °C, an indication error of +/-2 °C and a uniformity of +/-5 °C. The blast drying oven covers room temperature to 120 °C with the same fluctuation and indication error and a uniformity of +/-3 °C.

Two electronic balances are used, one with a scale interval of 0.0001 g and one with a scale interval of 0.00001 g. The film applicator has a blade height of 200 micrometres to 350 micrometres and the roller press a pressure range of 3 t/m to 5 t/m.

The remaining equipment is a sponge polishing rod, a punching machine, a coin cell

sealing machine and a planetary mixer.

6 Test procedure

Electrode sheets are prepared at a temperature of 25 °C +/- 2 °C and a relative humidity of not more than 50 %.

Four formulations are weighed out according to the type of negative electrode material, the ratios being mass fraction ratios and the binder figures being converted to solids: natural graphite, with sample, sodium carboxymethyl cellulose and styrene butadiene rubber at 96.5 to 1.5 to 2; artificial graphite, with sample, conductive carbon black, sodium carboxymethyl cellulose and styrene butadiene rubber at 95 to 1.5 to 1.5 to 2; silicon carbon, with sample, conductive carbon black and acrylonitrile multi-copolymer at 91 to 3 to 6; and carbon composite silicon monoxide, with sample, conductive agent made of conductive carbon black and conductive graphite, and acrylonitrile multi-copolymer at 75 to 15 to 10.

The weighed reagents and materials are mixed in a beaker under the planetary mixer until the slurry is pasty, with a solids content by mass of 40 % to 45 % and an even dispersion. The slurry is spread evenly on copper foil until the surface is smooth, laid flat on a glass plate, moved into the blast drying oven and dried at 95 °C to 105 °C for at least 2 h, giving a sheet with a single side areal density of 60 g/m2 to 100 g/m2.

The head 3 cm and the tail 2 cm of the sheet are cut away and the roll gap is adjusted; rolling stops once the compacted density reaches its design value, which is 1.45 g/cm3 to 1.65 g/cm3 for graphite negative electrode materials, 1.4 g/cm3 to 1.52 g/cm3 for silicon carbon and 1.3 g/cm3 to 1.5 g/cm3 for carbon composite silicon monoxide.

Enough discs of 6 mm to 16 mm diameter are punched from the rolled sheet and weighed accurately, then wrapped in weighing paper and aluminium foil, dried under vacuum at 110 °C to 130 °C for 6 h to 12 h, put into a parts box and moved to the argon glove box for storage. Ten discs of the same diameter are punched from a piece of bare copper foil and weighed accurately on the finer balance and their mean mass taken. The mass of active material in the coin cell is the difference between the mass of the electrode disc and the mean mass of the copper disc, multiplied by the mass fraction of active material in the weighed formulation. Note on the printed text: the legend of that equation gives the same wording, mass of the electrode sheet, for both the electrode disc and the copper disc symbols.

Coin cells are assembled at 25 °C +/- 2 °C with a moisture content of not more than 1 mg/m3 and an oxygen content of not more than 10 mg/m3, in the argon glove box, in the order from bottom to top: positive case, electrode disc, separator, lithium foil, nickel foam, spacer, spring support plate, negative case. The positive case is laid flat with its opening upward and kept free of dust; electrolyte is dropped in and the electrode disc placed with

tweezers so that the electrolyte holds it flat and centred; the separator is placed so that it covers the disc completely and is centred; more electrolyte is dropped on the centre of the separator and the lithium foil, polished smooth and free of burrs with the sponge rod, is placed, pressed lightly and centred; the nickel foam, then the spacer and the spring support plate are placed centred and aligned with one another; electrolyte is added to a total of 30 microlitres to 80 microlitres; the cell is moved to the sealing machine and crimped; and every assembled test cell is numbered and recorded.

The assembled cells are tested at 25 °C +/- 2 °C on the battery tester. For the first discharge specific capacity and the first coulombic efficiency the rate is 0.1C over a voltage range of 0.001 V to 1.5 V: the cell rests for 2 h, is discharged at constant current in a descending series of rates, 0.1C to 0.005 V and then 0.09C, 0.08C, 0.07C, 0.06C, 0.05C, 0.04C, 0.03C and 0.02C each to 0.001 V, rests 15 min, is charged at 0.1C to 1.5 V and rests 15 min again.

For the discharge capacity retention rate at different rates six cycles are run between 0.01 V and 1.5 V. The first cycle charges and discharges at 0.1C and the second at 0.2C; the third discharges at 0.2C and charges at 2C; the fourth charges and discharges at 0.2C; the fifth discharges at 1C and charges at 0.2C; and the sixth discharges at 2C and charges at 0.2C. Each constant current discharge to 0.01 V is followed by a constant voltage discharge until the current falls below 0.01C, and each step is separated by a rest of 15 min.

7 Calculation of results and test report

The first discharge specific capacity, in mAh/g, is the first discharge capacity at the 0.1C rate divided by the mass of active material in the coin cell. The first coulombic efficiency, as a percentage, is the ratio of the first charge specific capacity to the first discharge specific capacity, both at the 0.1C rate.

The discharge capacity retention rate is obtained from the specific capacity at the 2C rate and the specific capacity at the 0.2C rate and is expressed as a percentage. All three results are rounded to two decimal places in accordance with GB/T 8170.

Note on the printed text: in the legend of the retention rate equations the two symbols carrying the discharge subscript are described as the first charge specific capacity and the first charge capacity at the 2C rate, while the property being calculated is a discharge capacity retention rate. The wording is given here as it is printed.

The test report carries at least the sample name, the production batch number, the test date, time and place, the model of the instrument used and the operator; the analysis results and the way they are expressed; and any operation not included in the document or any freely chosen test condition.