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Determination method of carbon material - Part 2: Determination of expansion ratio

炭材料测定方法 第2部分:膨胀率的测定

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1 Scope and defined terms

The document describes the principle, the instruments and reagents, the test procedure, the analysis of results and the test report for the determination of the expansion ratio of carbon materials, and it applies to the determination of the coating expansion ratio of electrode materials for lithium-ion batteries such as artificial graphite, natural graphite, carbon composite silicon monoxide and silicon carbon. The one normative reference is GB/T 4369-2015 on lithium.

Expansion ratio is defined as the rate of change of the thickness of the material under stated experimental conditions. A first note adds that the expansion ratio is affected by the areal density of the electrode sheet; a second states that in this document it means the rate of change of the thickness of the electrode material coating on the electrode sheet of a coin lithium cell assembled from the carbon material, after twenty charge and discharge cycles.

Rolling density of the electrode is defined as the packing density on the electrode sheet reached when a negative electrode material for lithium-ion batteries, coated onto a foil by a particular method to make an electrode sheet, is then rolled in a roller press.

4 Principle and test conditions

The test sample is made into an electrode sheet, which is assembled under stated conditions into a coin cell or a mould cell of the same type. The cell is charged and discharged under stated conditions, the thickness of the electrode material coating on the sheet is measured before and after the cycling, and the change in thickness divided by the thickness before cycling is the expansion ratio of the carbon negative electrode material.

The test is carried out at a temperature of 23 °C +/- 5 °C and a relative humidity of not more than 60 %.

6 Reagents, materials and equipment

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. Sodium carboxymethyl cellulose, abbreviated CMC, has a viscosity of 3000 mPa.s to 5000 mPa.s at 25 °C on a 1 % solids solution and a pH of 6.0 to 8.5; styrene butadiene rubber, abbreviated SBR, 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 4369-2015 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 ethylene carbonate, dimethyl carbonate and ethyl methyl carbonate in the volume ratio 1 to 1 to 1. The coin cell components are the standard parts of a CR2016 or CR2032 cell, the spring support plate being absent from the CR2016.

The equipment is the same set as in part 1 of the series: a battery tester with a current and voltage accuracy of 0.05 % of reading plus 0.05 % of full scale; an argon glove box at one standard atmosphere with a total leak rate of not more than 5 x 10-4 per hour by volume; a vacuum drying oven below 100 Pa covering room temperature to 250 °C with a fluctuation and indication error of +/-2 °C and a uniformity of +/-5 °C; a blast drying oven covering room temperature to 120 °C with a uniformity of +/-3 °C; electronic balances with scale intervals of 0.0001 g and 0.00001 g; a film applicator with a blade height of 200 micrometres to 350 micrometres; a roller press with a pressure range of 3 t/m to 5 t/m; a sponge polishing rod; a punching machine; a coin cell sealing machine; and a planetary mixer.

Note on the printed text: the acrylonitrile multi-copolymer called up by two of the four formulations of the weighing subclause does not appear in the list of reagents and materials.

8 Test procedure

Electrode sheets are prepared at 25 °C +/- 2 °C and a relative humidity of not more than 50 %. The four formulations are weighed by mass fraction ratio, with the binder converted to solids: natural graphite, sample with sodium carboxymethyl cellulose and styrene butadiene rubber at 96.5 to 1.5 to 2; artificial graphite, sample with conductive carbon black, sodium carboxymethyl cellulose and styrene butadiene rubber at 95 to 1.5 to 1.5 to 2; silicon carbon, sample with conductive carbon black and acrylonitrile multi-copolymer at 91 to 3 to 6; and carbon composite silicon monoxide, sample with a conductive agent of conductive carbon black and conductive graphite and acrylonitrile multi-copolymer at 75 to 15 to 10.

The materials are mixed in a beaker under the planetary mixer until the slurry is pasty, with a solids content of 40 % to 45 % and an even dispersion, then spread evenly on copper foil until the surface is smooth, laid flat on a glass plate and dried in the blast oven at 95 °C to 105 °C for at least 2 h, giving a single side areal density of 60 g/m2 to 100 g/m2. Note on the printed text: the coating subclause refers back to the slurry of 6.1.3, a subclause number that belongs to part 1 of the series; the corresponding subclause of this part is 8.1.3.

For rolling, sheet 2 cm to 3 cm long is cut from each end and a piece about 2 cm long is taken from the rest. The roll gap is set and the sheet rolled; the rolled sheet is wrapped in clean paper such as weighing paper and a disc is punched from it with a 10 mm punch, and the mass and the thickness of that disc are measured and the compacted density of the coating calculated. The roll gap is then reset and further pieces rolled in the same way until the required sheet thickness is reached, when discs are punched again and four to six discs of close mass are chosen and their mass and thickness recorded. A note refers the compaction density control table and its calculation method to Annex A.

The small discs are wrapped in copper foil, put into the vacuum drying oven under a weight and dried for 8 h at 80 °C and a vacuum of 0.1 MPa, after which the sheet thickness is measured. A disc of the same diameter is punched from a piece of bare copper foil and the copper foil thickness measured.

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 sheet, separator, lithium foil, nickel foam, spacer, spring support plate, negative case. The steps are those of part 1 of the series: the positive case laid flat and kept free of dust, electrolyte dropped in and the sheet placed and centred with tweezers, the separator laid over it centred, more electrolyte on the centre of the separator and the lithium foil polished smooth with the sponge rod before being placed, pressed lightly and centred, then the nickel foam, the spacer and the spring support plate placed centred and aligned, a total of 30 microlitres to 80 microlitres of electrolyte added, and the cell crimped on the sealing machine.

The cycling test on the battery tester follows a fixed programme: a rest of 2 h; a constant current discharge at 0.1C to 0.01 V followed by a constant voltage discharge at 0.01 V until the current falls below 0.01C; a rest of 15 min; a charge at 0.1C to 1.5 V; a rest of 15 min; a constant current discharge at 0.5C to 0.01 V followed by a constant voltage discharge at 0.01 V until the current falls below 0.01C; a rest of 15 min; a charge at 0.5C to 1.5 V; then the sixth to the eighth step repeated as a cycle eighteen times; a rest of 15 min; and a final constant current discharge at 0.5C to 0.01 V followed by constant voltage discharge until the current falls below 0.01C.

After the test the cell is moved to the glove box and taken apart, the electrode sheet is removed, and its thickness is measured with a micrometer at four points, shown as red dots in Figure 1. One outlying thickness value is discarded and the mean of the rest is taken as the sheet thickness after cycling.

9 Calculation of results and test report

The coating thickness after vacuum drying is the dried sheet thickness less the copper foil thickness, and the coating thickness after cycling is the sheet thickness after cycling less the copper foil thickness, both in micrometres. The expansion ratio is the difference between the two coating thicknesses divided by the coating thickness after vacuum drying, expressed as a percentage.

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.

A Annex A (informative) Compaction density control table and calculation formula

The compacted density of the electrode sheet is calculated on the thickness after vacuum drying. Table A.1 gives the control values and has five columns: the mass of the electrode sheet disc in mg, the sheet thickness after rolling, the sheet thickness at weighing and the sheet thickness after drying, all three in micrometres, and the compacted density of the coating on the sheet in g/cm3.

The table has two rows. The first reads: disc mass from 11.84 up to but not including 11.92 mg; thickness after rolling below 46.5 micrometres; thickness at weighing from 48.0 up to but not including 48.5 micrometres; thickness after drying from 48.5 up to but not including 49.5 micrometres; compacted density from 1.53 up to but not including 1.59 g/cm3. The second reads: disc mass from 11.92 to 12.00 mg; thickness after rolling from 46.5 to 47.0 micrometres; thickness at weighing from 48.5 to 49.0 micrometres; thickness after drying from 49.0 to 50.5 micrometres; compacted density from 1.51 to 1.57 g/cm3.