Research on energy densities of secondary batteries

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Abstract. Improving the energy densities of secondary batteries has always been the core goal of scientific research and engineering development. In this paper, by testing the energy densities of the test samples, the gravimetric energy density (GED) and volumetric energy density (VED) of Li-ion and Li-metal batteries are analyzed. By comparing with the development trend of batteries at home and abroad, we can see that Li-metal batteries are the development direction of high-energy-density batteries in the future. By comparing the test results of this paper with the energy densities data published at home and abroad, we can see that the GED and VED of Li-ion and Li-metal batteries in China have reached the international advanced level. The research results of this paper can basically reflect the development status and provide guidance for the development of high-energy-density batteries in China.

1. Introduction

In recent years, with the rapid development of electronic products represented by mobile phones, the upgrading of electronic products is faster and faster, and the market competition is becoming increasingly fierce. With the function complexity and volume miniaturization of electronic products, the power consumption of electronic products is also increasing, which leads to the problem of battery endurance. At present, the batteries used in electronic products are basically lithium-ion batteries. The GED of single cell is basically below 300 Wh/kg, and the VED is basically below 600 Wh/L. The kind of battery cannot meet the market demand, so it is urgent to find a new kind of secondary battery with higher energy densities.

As an efficient and recyclable energy storage method, batteries with high energy densities have become the key supporting technology in almost all high-tech fields. Improving the energy density of the batteries has always been the core goal of scientific research and engineering development.

Although China is currently in the leading position in the production capacity of lithium-ion batteries in the world, there are still many places to learn from countries that master advanced science and technology in the development and basic research of new battery materials, new systems, new products, new technologies and new equipment. In the future, the core competitiveness of battery technology will inevitably come from the advanced battery technology with original innovation and continuous improvement of comprehensive technical indicators.

Through the research on the energy density of secondary batteries, we can find out the technical level of the energy density in China. By comparing the energy density with that of foreign countries, we can understand the gap between them and provide guidance for the development direction of high-energy-density batteries in China.
2. Test methods
The research samples of this paper are 34 batches of high GED/VED cells collected from universities, scientific research institutes, science and technology enterprises in a national competition project.

The core index of high-energy-density batteries is energy density, including GED and VED. Therefore, the test items in this paper are GED and VED.

According to the requirements of the sample provider, some samples only test GED (11 batches in total), some samples only test VED (9 batches in total), and some samples test both GED and VED (14 batches in total).

2.1. Environment condition
The ambient temperature: 25°C±2°C, the relative humidity: 25%~75%, the atmospheric pressure: 86kpa~106kpa.

2.2. Test procedure

2.2.1. Cell mass test
The cell mass (including the terminal lug, aluminum shell cell includes bolt connector and other necessary components; excluding the external clamp) was obtained by placing the cell on the calibrated electronic balance (accuracy ± 0.1%, kg). Each cell is measured three times and the average value is the final mass of the test cell.

2.2.2. Cell volume test
The volume test was carried out by drainage method. Put the container on the precision electronic balance (the precision is ± 0.1%, kg), inject the liquid into the container to a certain depth, and read the weight M₁ from the electronic balance. Clamp the cell lug and control the hanging line to make the cell enter the liquid slowly until the upper edge of the cell is level with the reference line. The clamp and hanging line cannot contact the liquid. The cell is suspended in the solution, it means the cell cannot contact the wall or bottom of the cup. The liquid cannot overflow from the container. Read the weight M₂ from the electronic balance. The difference between M₂ and M₁ is the mass of the discharged liquid, that is, m=M₂-M₁. In addition, m=V×ρ, V is the volume of the discharged liquid, that is also the volume of the cell; ρ is the density of the liquid. According to the formula, V=(M₂-M₁)/ρ×10⁻³, the cell volume V (L) was calculated.

2.2.3. GED/VED test
(1) The test cell shall be stored for 2 h at 25°C±2°C;
(2) The sample is then discharged at 25°C±2°C, at a constant current of 0.2C, down to the final voltage specified by the manufacturer. Then it shall be stored for 1 h;
(3) The sample is then charged at 25°C±2°C, at a constant current of 0.2C and a constant voltage specified by the manufacturer until the cut-off current is 0.05C. Then it shall be stored for 1 h;
(4) Repeat step (2);
(5) Repeat steps (3) ~ (4) 5 times, record the discharge energy E_d1~E_d5(Wh) respectively;
(6) Calculate the average discharge energy of the last three cycles, E_d(Eh)=(E_d3+E_d4+E_d5)/3;
(7) According to the formula, E_dM=E_d/M, calculate the GED of the test cell;
(8) According to the formula, E_dL=E_d/V, calculate the VED of the test cell.

2.3. Instrument and equipment
The main instruments and equipment used in this test are shown in Table 1.
Table 1. Main instruments and equipment

| Name                          | Model          | Manufacture       | Note                                                                 |
|-------------------------------|----------------|-------------------|----------------------------------------------------------------------|
| High precision battery test   | LBT21084-0-20  | Arbin Corporation | Range: (0~20)V/(0~10)A; Accuracy: ±0.02%FSR; Fastest sampling accuracy: 10ms. |
| Precision electronic balance | JA-1200        | NAPCO             | Range: 0~1.2kg; Accuracy: ±0.01%, kg                                  |

3. Test results and analysis

According to the chemical system classification, 34 batches of the cell samples can be divided into lithium-ion system (17 batches in total) and lithium metal system (17 batches in total). According to the basic information provided by the sample provider, the positive materials of the lithium-ion samples include lithium cobalt, lithium titanate, high nickel ternary materials, lithium rich manganese based materials, etc., and the negative materials include graphite and graphene materials; Among the lithium metal samples, the positive materials include sulfur, lithium rich manganese base materials, transition metal oxides, lithium cobalt and NCM materials, etc., the negative material is lithium metal. It can be inferred that the current domestic research on high-energy-density batteries mainly focuses on lithium-ion and lithium metal batteries.

The GED and VED of the 34 batches of cell samples were tested according to the unified test methods. The test results were classified according to lithium-ion system and lithium metal system, and the data of each group were arranged from small to large. The statistical test results are shown in Table 2.

Table 2. Test data of GED/VED

| Number | Lithium-ion system | Lithium metal system |
|--------|--------------------|----------------------|
|        | GED(Wh/kg) | VED(Wh/L) | GED(Wh/kg) | VED(Wh/L) |
| 1      | 89.0       | 2.5*     | 0*         | 12.0*     |
| 2      | 264.4      | 195.5    | 118.4      | 675.9     |
| 3      | 265.4      | 639.9    | 323.0      | 797.0     |
| 4      | 266.3      | 642.3    | 414.0      | 1031.0    |
| 5      | 285.4      | 643.1    | 447.7      | 1067.1    |
| 6      | 289.3      | 681.8    | 447.9      | 1194.6    |
| 7      | 294.2      | 735.0    | 456.3      | 1213.5    |
| 8      | 297.2      | 737.1    | 475.0      | 1483.8    |
| 9      | 301.3      | 738.1    | 502.0      | 1704.2    |
| 10     | 320.3      | 750.0    | 510.8      | 1834.6    |
| 11     | 338.5      | 842.7    | 533.5      | /         |
| 12     | 355.2      | 873.7    | 545.2      | /         |
| 13     | 423.1      | 894.7    | /          | /         |

Note: The test data at the mark "*" indicates that the test results are abnormal and the test sample cannot discharge normally.

According to the test data in Table 1, the max. GED and VED of lithium-ion samples are 423.1 Wh/kg and 894.7 Wh/L respectively. The max. GED and VED of the lithium metal samples are 545.2 Wh/kg and 1834.6 Wh/L respectively, which is also the max. GED and VED of the total 34 batches of cell samples in this paper.

The GED and VED data of the two chemical systems are plotted and compared respectively: serial
number 1-13 is taken as abscissa (only used to distinguish different data points), GED and VED are taken as ordinate. The test data marked with "*" is eliminated and not shown in the figure. The obtained graphs are shown in Fig. 1 and Fig. 2.

It can be seen from Fig. 1 that, the GED of lithium metal samples is obviously better than that of lithium-ion samples, the former is concentrated in the range of (400-550) Wh/kg, and the latter is concentrated in the range of (250-400) Wh/kg, as shown by the blue dotted line in Fig. 1.

It can be seen from Fig. 2 that, the VED of lithium metal samples is also significantly better than that of lithium-ion samples, the former is concentrated in the range of (900-1900) Wh/L, and the latter is concentrated in the range of (600-900) Wh/L, as shown by the blue dotted line in Fig. 2.
From the analysis of test results, it can be seen that the GED and VED of the lithium metal samples are superior to those of the lithium-ion samples. It can be concluded that the research of today on high-energy-density batteries mainly focuses on lithium-ion system and lithium metal system, and the lithium metal system is the development direction.

4. Comparison at home and abroad

According to the relevant literature [1-8], the development trend of high-energy-density batteries at home and abroad is basically the same, that is, from the lithium-ion system in today, near-term future and mid-term future, to the lithium metal system in long-term future, and then to other metal systems in more distant future, as shown in Fig. 3.

According to the chemical system of the test samples, the chemical system of the test cells covers that of today, near-term future, mid-term future and long-term future in Fig. 3. It can be concluded that both the lithium-ion system and lithium metal system represent the development direction of high-energy-density batteries at home and abroad in the future.

For lithium-ion batteries, the energy density published of today has reached 295 Wh/kg and 750 Wh/L\[^{[9-12]}\]. The expected target in 2025 is 400 Wh/kg and 1000 Wh/L\[^{[9-12]}\]. Combined with the test results of this paper, the GED and VED of the lithium-ion samples have reached 423.1 Wh/kg and 894.7 Wh/L respectively. It can be seen that the max. GED and VED of the lithium-ion samples have exceeded the published values of today, more than that, the max. GED has exceeded the expected target in 2025, which indicates that China's lithium-ion batteries are at the international leading level in these two parameters.

For lithium metal batteries, the GED published of today has reached 609 Wh/kg (S/Li battery)\[^{[13]}\] in China, which is equivalent to the international level. The predicted energy densities of lithium metal batteries can reach 1311 Wh/kg (S/Li battery) and 1900 Wh/L (CuF\(_2\)/Li battery)\[^{[9]}\]. Combined with the test results of this paper, the GED and VED of the lithium metal samples have reached 545.2 Wh/kg and 1834.6 Wh/L respectively. It can be seen that the max. VED of the lithium metal samples is very close to the estimated value, which indicates that China's lithium mental batteries are at the international leading level in VED; The max. GED is close to the current published value 609 Wh/kg, which also indicates that China's lithium mental batteries are equivalent to the international level in
GED. But there is still a certain gap from the estimated value 1311 Wh/kg, which indicates that the GED of lithium metal batteries in China needs to be further improved.

5. Conclusion
From the test results and analysis, it is found that the GED and VED of lithium metal batteries are obviously superior to that of lithium-ion batteries. Compared with the development trend of batteries at home and abroad, it is known that lithium metal batteries are the development direction of high-energy-density batteries in the future.

In addition, by comparing the test results of this paper with the published GED/VED data at home and abroad, we can see that the GED and VED of lithium-ion and lithium metal batteries in China have reached the international advanced level.

In conclusion, the test results of this paper can basically reflect the development status of high-energy-density batteries in China.

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